A CORRELATED TREATMENT OF BOUND-CONTINUUM TRANSITIONS WITHIN THE ELECTRON PROPAGATOR FORMALISM

BY

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To

My Parents

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A CORRELATED TREATMENT OF BOUND-CONTINUUM TRANSITIONS WITHIN THE ELECTRON PROPAGATOR FORMALISM

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A super-operator formulation for decoupling the symmetry blocks of the full 2p-h TDA electron propagator matrix is presented. The accuracy of this decoupling is explored by using the full 2p-h TDA overlap amplitudes to calculate relative ionization intensities for N_2 and H_2O. The effect of excluding orbitals on the calculated ionization potentials and relative ionization cross-sections is reported. The use of intensities obtained from successively larger subsets for labeling the photoelectron spectrum is suggested.

Expressions are formulated for the correlated treatment of photoionization cross-sections using Feynman-Dyson amplitudes of the electron propagator to describe the ionization processes and an orthogonalized plane wave description for the photoelectron. Explicit equations are derived for the theoretical treatment of experimental cross-sections using either spherical grid deflection type spectrometers or those using a particular collection angle. A scheme is suggested for systematic improvement of the theoretical description.

A dilated electron propagator for the direct calculation of resonance energies and widths for quasi-bound anions of closed shell atoms is proposed. The treatment employs creation and annihilation operators defined on bi-variationally obtained bi-orthogonal orbital basis set. Explicit equations for the dilated electron propagator correct through second order in electron interaction are presented. Higher order and renormalized treatments are suggested and the details of a computational strategy outlined. The bi-variational SCF scheme for dilatated closed shell atomic Hamiltonians is studied and discussed. Applications to the Be atom are presented.

INTRODUCTION

The bound-continuum transitions which involve the ejection of electrons from bound states into continuum or the attachment of electrons in the continuum to bound or quasi-bound states, due to the quantal nature of their energetics, provide a definitive insight into the electronic structure and dynamics of atoms and molecules. Since the attachment or detachment of electrons may lead to substantial realignment of interelectronic interactions, the independent particle schemes which take account of these interactions only in a particular average way are not always satisfactory. As such, correlated treatments of bound-continuum transitions which allow for dynamic correlation of interelectronic interactions are of paramount importance in attempting a theoretical description of chemical phenomena.

In its spectral representation, poles of the electron propagator (Linderberg and Öhrn, 1973)

$$\underline{G}_{pq}(E) = \lim_{\eta \to 0} \sum_{s} \left[\frac{f_s(p) f_s^*(q)}{E - \{E_s(N+1) - E_0(N)\} + i\eta} + \frac{g_s(p) g_s^*(q)}{E - \{E_0(N) - E_s(N-1)\} - i\eta} \right]$$

where Feynman-Dyson overlap amplitudes f_s and g_s are defined as

$$f_s(p) = \langle N | a_p | N+1, s \rangle$$

$$g_s(p) = \langle N-1, s | a_p | N \rangle$$

permit the direct calculation of transition energies involved in attachment $\{E_s(N+1)-E_0(N)\}$ and detachment $\{E_0(N)-E_s(N-1)\}$ of electrons in atoms and molecules. The dynamic correlation of inter-electronic interactions is incorporated through summation over all possible (N+1,s) or (N-1,s) electron states that can emerge from the initial ground state of energy $E_0(N)$. Other correlated treatments of bound-continuum transitions necessitate the calculation of total energy for both ground $\{E_0(N)\}$ and the final state $\{E(N+1)$ or $E(N-1)\}$, and transition energy is calculated as the difference. These latter methods suffer from the significant loss of accuracy inherent in the subtraction of two nearly equal total energies to obtain a much smaller transition energy. Also, the approximations resorted to for computational tractability of these methods do not always lend themselves to cogent mathematical formulations. Care must also be taken to avoid disparate levels of approximating electron correlation in the calculation of each state. The electron propagator formalism does not suffer from these defects, and various approximations lend themselves to systematic improvement. This has prompted us to formulate theoretical schemes which should make possible an accurate treatment of bound-continuum transitions using the electron propagator formalism in conjunction with the ideas of dilated hamiltonians (Aguilar and Combes, 1971; Balslev and Combes, 1971; Simon, 1972).

The causal electron propagator (Linderberg and Öhrn, 1973; Simons, 1976)

$$G(x,x',\tau) = -i\theta(\tau)\langle\psi(x,\tau)\psi^\dagger(x',0)\rangle + i\theta(-\tau)\langle\psi^\dagger(x',0)\psi(x,\tau)\rangle$$

where $\theta(\tau)$ is the Heaviside step function, and $\psi,\psi^\dagger$ are the electron field operators in the Heisenberg representation. The brackets define a ground state average relative to some normalized density operator ρ

$$<\psi(x,\tau)\psi^{\dagger}(x',0)> \;=\; \mathrm{Tr}\{\rho\psi(x,\tau)\psi^{\dagger}(x',0)\}$$

Introducing a discrete, orthonormal set of spin orbitals $\{u_k(x)\}$, the electron field operators can be expanded in a set of spin orbital annihilation and creation operators.

$$a_s(\tau) \;=\; \int u_s^*(x)\psi(x,\tau)dx$$

In this representation the electron propagator is expressed as a matrix with the elements

$$\underline{G}_{sr}(\tau) \;=\; -i\theta(\tau)<a_s(\tau)a_r^{\dagger}(0)> \;+\; i\theta(-\tau)<a_r^{\dagger}(0)a_s(\tau)>$$

The Fourier transform of the electron propagator satisfies the following equation of motion:

$$\begin{aligned}\underline{G}_{sr}(E) \;=\; & E^{-1}<[a_s,a_r^{\dagger}]_+> \;+\; E^{-2}<[[a_s,H]_-,a_r^{\dagger}]_+> \;+\\ & E^{-3}<[[[a_s,H]_-,H]_-,a_r^{\dagger}]_+> \;+\; \ldots\end{aligned}$$

where H is the Hamiltonian

$$H \;=\; \sum_{r,s} h_{rs}a_r^{\dagger}a_s \;+\; \tfrac{1}{4}\sum_{rr',ss'} <rr'||ss'>a_r^{\dagger}a_{r'}^{\dagger}a_{s'}a_s$$

and

$$<rr'||ss'> \;=\; \int u_r^*(1)u_{r'}^*(2)r_{12}^{-1}(1-P_{12})u_s(1)u_{s'}(2)d\tau_1 d\tau_2$$

By introducing a linear space $\underline{L} = \{a_i,\ a_k^{\dagger}a_{\ell}a_m(\ell<m),\ \ldots\}$ of fermion like field operators which supports a scalar product

$$(X_i|X_j) \;=\; \mathrm{Tr}\{\rho[X_i^{\dagger},X_j]_+\}, \qquad X_i,\ X_j \in \underline{L}$$

by defining the identity superoperator $\hat{I}$ and the Hamiltonian superoperator $\hat{H}$ as

$$\hat{I}X = X$$
$$\hat{H}X = [X,H]_- \qquad X \in \underline{L}$$

and, finally, by arranging the annihilation operators in a row vector and the creation operators in a column vector, the equation of motion for the Fourier transformed causal electron propagator may be recast as (Goscinski and Lukman, 1970; Pickup and Goscinski, 1973)

$$\underline{G}(E) = (\underline{a}|(E\hat{I}-\hat{H})^{-1}\underline{a})$$

which may be approximated via the inner-projection technique (Löwdin, 1965) as

$$\underline{G}(E) \simeq (\underline{a}|\underline{h})(\underline{h}|(E\hat{I}-\hat{H})\underline{h})^{-1}(\underline{h}|\underline{a})$$

where the choice of projection manifold $\underline{h}$ defines a particular approximation to the electron propagator.

In chapter one we describe the use of symmetry adapted linear combination of annihilation and creation operator products to decouple the symmetry blocks of the electron propagator matrix. We demonstrate its use for making manageable the computation of transition energies for ionization processes using the Tamm-Dancoff approximation (TDA). These results are used for comparative investigation of TDA and other approximants (Mishra and Öhrn, 1980a).

The necessary formalism for the use of Feynman-Dyson amplitudes of the electron propagator for correlated treatment of photoionization cross-sections is fabricated in chapter two (Mishra and Öhrn, 1980b).

The results of cross-section calculations using this formalism with plane wave approximation for the photoelectron are used for further examination of the TDA propagator.

In chapter three, the electron propagator equations are generalized to permit the description of transitions involving quasi-bound states described by non-hermitian Hamiltonians. The use of this more general dilated electron propagator (Mishra, Froelich and Öhrn, 1980) for a unified treatment of all bound-continuum transitions involving bound states or quasi-bound states for the calculation of ionization energy, electron affinity, shape, and Feshbach resonances (Taylor, 1970) for atoms and molecules is adumbrated, and the results for zeroth order dilated electron propagator (Mishra, Öhrn and Froelich, 1980) are analyzed and discussed in this chapter.

CHAPTER 1

BOUND CONTINUUM TRANSITIONS WITHIN 2p-h TAMM-DANCOFF APPROXIMATION

1.1 The 2p-h Tamm-Dancoff Approximation, (2p-h TDA)

We have noted earlier that, in the superoperator formulation (Goscinski and Lukman, 1970; Pickup and Goscinski, 1973), the electron propagator matrix is given by

$$\underline{G}(E) = (\underline{a}|(E\hat{I}-\hat{H})^{-1}\underline{a}) \tag{1.1}$$

which may be approximated via the inner projection technique (Löwdin, 1965)

$$\underline{G}(E) \approx (\underline{a}|\underline{h})(\underline{h}|(E\hat{I}-\hat{H})\underline{h})^{-1}(\underline{h}|\underline{a}) \tag{1.2}$$

It has been shown (Born and Öhrn, 1979) that the choice of projection manifold $\underline{h}$ as

$$\underline{h} = \underline{h}_1 \oplus \underline{h}_3 \tag{1.3}$$

where

$$\underline{h}_1 = \{a_i\}$$

$$\underline{h}_3 = \{h_{k\ell m}\}$$

$$h_{k\ell m} = N_{k\ell m}^{-\frac{1}{2}}\{a_k^{+}a_\ell a_m + \delta_{km}\langle n_k\rangle a_\ell - \delta_{k\ell}\langle n_k\rangle a_m\}$$

$$N_{k\ell m} = n_k\{(1-\langle n_\ell\rangle-\langle n_m\rangle) + \langle n_\ell\rangle\langle n_m\rangle\}$$

$\langle n_k\rangle$ = occupation number for the spin orbital k leads to what has been labelled as the 2p-h (2 particle-hole) Tamm-Dancoff Approximation (Schirmer and Cederbaum, 1978a).

With this choice of the projection manifold, the electron propagator may be written as

$$\underset{=}{G}^{-1}(E) = (\underline{h}_1|E\hat{I}-\hat{H})\underline{h}_1) - (\underline{h}_1|\hat{H}\underline{h}_3)(\underline{h}_3|(E\hat{I}-\hat{H})\underline{h}_3)^{-1}(\underline{h}_3|\hat{H}\underline{h}_1) \quad (1.4)$$

$$= \underset{=}{G}_0^{-1} - \underset{=}{\Sigma} \quad (1.5)$$

where

$$\underset{=}{\Sigma} = (\underline{h}_1|\hat{H}\underline{h}_3)(\underline{h}_3|(E\hat{I}-\hat{H})\underline{h}_3)^{-1}(\underline{h}_3|\hat{H}\underline{h}_1) \quad (1.6)$$

is the so-called self-energy matrix (Dyson, 1949).

The computational bottleneck in implementing the full 2p-h TDA and other self-energy approximants has been the size of the $h_{k\ell m}$ manifold ($\simeq M^3$, where M is the size of the basis) and the consequent enormity of the matrix inversion problem in eq. (1.6). Previously, this has necessitated the approximation of the inverse matrix in (1.6) by its diagonal elements (the diagonal 2p-h TDA) or the approximation of $\hat{H}$ in the inverse matrix by $\hat{H}_0$ (the second order approximation). These approximations obliterate correlation effects which provide a deeper insight into the electronic structure of chemical systems, e.g. a breakdown of the orbital picture of ionization for the inner valence orbitals (Schirmer and Cederbaum, 1978b; Mishra and Öhrn, 1980a).

In the next section, we describe the use of symmetry adapted linear combination of the operator products in the $\underline{h}_3$ manifold to reduce the size of the matrix inversion problem by decoupling the evaluation of electron propagator matrix into those of its smaller symmetry blocks. This makes possible the evaluation of the full 2p-h TDA propagator.

While the explicit use of this technique has been made only for the reduction of the $h_{k\ell m}$ manifold into its invariant subspaces, the $\underline{h}_5 = \{a_j^\dagger a_k^\dagger a_\ell a_m a_n,\ j<k;\ \ell<m<n\}$ manifold may also be reduced to introduce significant savings in the higher order decouplings of the electron propagator (Redmon, Purvis and Öhrn, 1975).

1.2 Decoupling of the Symmetry Blocks of the 2p-h TDA Propagator

The reduction of $h_{k\ell m}$ manifold may be achieved by using the decomposition

$$\underline{h}_3 = \sum_i \oplus \underline{h}_3^i \tag{1.7}$$

where the summation is over all the irreducible representations of the molecular point group, and the irrep i of $h_{k\ell m}^i$ is given by

$$i = \text{ksym} \otimes \ell\text{sym} \otimes \text{msym} \tag{1.8}$$

ksym, ℓsym, and msym being symmetry labels for the orbitals k, ℓ and m obtained from the SCF procedure. We limit ourselves to those point groups which have only one dimensional irreducible representations.

Obviously

$$\underline{h}_1 = \sum_i \oplus \underline{h}_1^i \tag{1.9}$$

This affords the rewriting of $\underline{\Sigma}(E)$ as

$$\underline{\Sigma}(E) = \sum_i \oplus \underline{\Sigma}^i(E) \tag{1.10}$$

where

$$\underline{\Sigma}^i(E) = (\underline{h}_1^i|\hat{H}\underline{h}_3^i)(\underline{h}_3^i|(E\hat{I}-\hat{H})\underline{h}_3^i)^{-1}(\underline{h}_3^i|\hat{H}\underline{h}_1^i) \tag{1.11}$$

We further reduce the size of the problem by realizing that the creation and annihilation operators are tensor operators of rank ½ with respect to the spin angular momentum, and as such, the following decomposition

$$\underline{h}_3^i \;=\; \underline{q}^i \oplus \underline{f}^i \oplus \underline{d}^i \tag{1.12}$$

may be achieved by using the Wigner-Racah Tensor calculus (Linderberg and Öhrn, 1973; Messiah, 1958) whereby

$$\left(a^+_{k\kappa}\left(\bar{a}_{\ell\lambda}\bar{a}_{m\mu}\right)^{s'}_{M_{s'}}\right)^{s}_{M_s} \tag{1.13}$$

$$= (-)^{s'-\frac{1}{2}-M_s}\sum_{\kappa,M_{s'},\lambda,\mu}(-)^{M_{s'}}(2s'+1)^{\frac{1}{2}}(2s+1)^{\frac{1}{2}}\begin{pmatrix}\frac{1}{2} & \frac{1}{2} & s'\\ \lambda & \mu & -M_{s'}\end{pmatrix}$$

$$\times\begin{pmatrix}\frac{1}{2} & s' & s\\ \kappa & M_{s'} & -M_s\end{pmatrix}a^+_{k\kappa}\bar{a}_{\ell\lambda}\bar{a}_{m\mu}$$

$$\bar{a}_{m\mu} \;=\; (-)^{\frac{1}{2}-\mu}a_{m-\mu} \tag{1.14}$$

$$(q_{k\ell m})^{3/2}_{3/2} \;\equiv\; (a^+_{k\kappa}\bar{a}_{\ell\lambda}\bar{a}_{m\mu})^{3/2}_{3/2} \;=\; N^{-\frac{1}{2}}_{k\ell m}a^+_{k\alpha}a_{\ell\beta}a_{m\beta} \tag{1.15}$$

$$(q_{k\ell m})^{3/2}_{1/2} \;\equiv\; (a^+_{k\kappa}\bar{a}_{\ell\lambda}\bar{a}_{m\mu})^{3/2}_{1/2} \;=\; \frac{N^{-\frac{1}{2}}_{k\ell m}}{\sqrt{3}}\{a^+_{k\beta}a_{\ell\beta}a_{m\beta}-a^+_{k\alpha}a_{\ell\beta}a_{m\alpha}$$

$$-a^+_{k\alpha}a_{\ell\alpha}a_{m\beta}\} \tag{1.16}$$

$$(q_{k\ell m})^{3/2}_{-\frac{1}{2}} \;\equiv\; (a^+_{k\kappa}\bar{a}_{\ell\lambda}\bar{a}_{m\mu})^{3/2}_{-\frac{1}{2}} \;=\; \frac{N^{-\frac{1}{2}}_{k\ell m}}{\sqrt{3}}\{a^+_{k\alpha}a_{\ell\alpha}a_{m\alpha}-a^+_{k\beta}a_{\ell\alpha}a_{m\beta}$$

$$-a^+_{k\beta}a_{\ell\beta}a_{m\alpha}\} \tag{1.17}$$

$$(q_{k\ell m})^{3/2}_{-3/2} \;\equiv\; (a^+_{k\kappa}\bar{a}_{\ell\lambda}\bar{a}_{m\mu})^{3/2}_{-3/2} \;=\; N^{-\frac{1}{2}}_{k\ell m}a^+_{k\beta}a_{\ell\alpha}a_{m\alpha} \tag{1.18}$$

$$f_{k\ell m} \equiv (a^{+}_{k\kappa}(\bar{a}_{\ell\lambda}a_{m\mu})^{0}_{0})^{\frac{1}{2}}_{\frac{1}{2}} = \frac{N^{-\frac{1}{2}}_{k\ell m}}{\sqrt{2}}\{a^{+}_{k\alpha}a_{\ell\beta}a_{m\alpha}-a^{+}_{k\alpha}a_{\ell\alpha}a_{m\beta}-\delta_{k\ell}<n_{k}>a_{m\beta}$$

$$-\delta_{km}<n_{k}>a_{\ell\beta}\} \qquad \ell < m \quad (1.19)$$

$$= N^{-\frac{1}{2}}_{k\ell m}\{a^{+}_{k\alpha}a_{\ell\beta}a_{\ell\alpha}-\delta_{k\ell}<n_{k}>a_{\ell\beta}\} \quad (1.20)$$

$$\ell = m$$

$$d_{k\ell m} \equiv (a^{+}_{k\kappa}(\bar{a}_{\ell\lambda}\bar{a}_{m\mu})^{1}_{M_{s'}})^{\frac{1}{2}}_{\frac{1}{2}} = \frac{N^{-\frac{1}{2}}_{k\ell m}}{\sqrt{6}}\{2a^{+}_{k\beta}a_{\ell\beta}a_{m\beta}+a^{+}_{k\alpha}a_{\ell\beta}a_{m\alpha}$$

$$+a^{+}_{k\alpha}a_{\ell\alpha}a_{m\beta}-3\delta_{k\ell}<n_{k}>a_{m\beta}$$

$$+3\delta_{km}<n_{k}>a_{\ell\beta}\} \qquad \ell < m \quad (1.21)$$

In further discussions we drop the superscript for the irrep of the point group, since the reduction of the projection manifold has uncoupled the different symmetry blocks, and we treat them separately. Thus, for every symmetry block

$$\underline{\Sigma}(E) = [(\underline{a}|\hat{v}\underline{q})(\underline{a}|\hat{v}\underline{f})(\underline{a}|\hat{v}\underline{d})] \begin{bmatrix} (\underline{q}|(E\hat{I}-\hat{H})\underline{q})(\underline{q}|(E\hat{I}-\hat{H})\underline{f})(\underline{q}|(E\hat{I}-\hat{H})\underline{d}) \\ (\underline{f}|(E\hat{I}-\hat{H})\underline{q})(\underline{f}|(E\hat{I}-\hat{H})\underline{f})(\underline{f}|(E\hat{I}-\hat{H})\underline{d}) \\ (\underline{d}|(E\hat{I}-\hat{H})\underline{q})(\underline{d}|(E\hat{I}-\hat{H})\underline{f})(d|(E\hat{I}-\hat{H})\underline{d}) \end{bmatrix}^{-1} \begin{bmatrix} (\underline{q}|\hat{v}a) \\ (\underline{f}|\hat{v}\underline{a}) \\ (\underline{d}|\hat{v}\underline{a}) \end{bmatrix}$$

$$(1.22)$$

and since

$$(\underline{a}|\hat{v}\underline{q}),\ (\underline{q}|\hat{v}\underline{a}),\ (\underline{f}|(E\hat{I}-\hat{H})\underline{q}),\ (\underline{d}|(E\hat{I}-\hat{H})\underline{q}),\ (\underline{q}|(E\hat{I}-\hat{H})\underline{f}),$$
$$(\underline{q}|(E\hat{I}-\hat{H})\underline{d}) \quad (1.23)$$

are null matrices,

$$\underline{\Sigma}(E) = [(\underline{a}|\hat{v}\underline{f})(\underline{a}|\hat{v}\underline{d})] \begin{bmatrix} (\underline{f}|(E\hat{I}-\hat{H})\underline{f})(\underline{f}|(E\hat{I}-\hat{H})|\underline{d}) \\ (\underline{d}\ (EI-H)\underline{f})(\underline{d}\ (EI-H)\ \underline{d}) \end{bmatrix}^{-1} \begin{bmatrix} (f|\hat{v}\underline{a}) \\ (\underline{d}\ v\underline{a}) \end{bmatrix} \quad (1.24)$$

Diagonalization of the blocked inverse matrix of Eq. 1.24 leads to

$$\Sigma_{ij}(E) = \sum_n \frac{m_i(n)m_j^*(n)}{E-\mu_n} \qquad (1.25)$$

Detailed expressions for $m_i(n)$ and μ_n in terms of two-electron integrals and orbital energies may easily be obtained using relations provided by Born and Öhrn (1979) employing the HF density operator and integral occupation numbers. These are identical to those of Schirmer and Cederbaum (1978a).

1.3 Comparison of the Full 2p-h TDA and Other Self-energy Approximants

As introduced earlier, the electron propagator in its spectral representation is given as (Linderberg and Öhrn, 1973).

$$\underline{G}_{pq}(E) = \lim_{\eta\to 0+} \sum_s \left\{\frac{f_s(p)f_s^*(q)}{E+E_0(N)-E_s(N+1)+i\eta} + \frac{g_s(p)g_s^*(q)}{E+E_s(N-1)-E_0(N)-i\eta}\right\} \qquad (1.26)$$

The quantities needed for the comparison of different decouplings are the ionization energies and the Feynman-Dyson overlap amplitudes f_s and g_s defined as

$$f_s(p) = \langle N|a_p|N+1,s\rangle \qquad (1.27)$$

$$g_s(p) = \langle N-1,s|a_p|N\rangle \qquad (1.28)$$

Schirmer and Cederbaum (1978b) have used the full 2p-h Tamm-Dancoff Approximation to the electron propagator to investigate the inner valence ionization of several molecules and have compared its accuracy with the diagonal approximations. An interesting feature that has emerged from their investigations is the complete breakdown of the orbital picture of ionization for the inner valence orbitals. However, their comparative investigation of the full 2p-h TDA has been done using only a subset of the one particle orbitals (Schirmer and Cederbaum, 1978b; Cederbaum et al., 1978) and by comparing the poles of the propagator with experimental and other theoretical values for the ionization energies. This criterion represents a particular bias, since it does not reflect the quality of the overlap amplitudes. The Feynman-Dyson amplitudes determine the spectral density function (Linderberg and Öhrn, 1973),

$$A(x,x';E) = \begin{cases} \sum_k f_k(x) f_k^*(x') \delta(E-E_k) & E > \mu \\ \sum_k g_k(x) g_k^*(x') \delta(E-E_k) & E \leq \mu \end{cases} \tag{1.29}$$

where the parameter μ in this case is the chemical potential of the N-electron ground state. Since a good deal of important information can be extracted from the spectral density function, e.g. the one-particle reduced density matrix (Linderberg and Öhrn, 1973),

$$\gamma(x,x') = \int_C A(x,x';E)dE \tag{1.30}$$

it is important to choose a decoupling approximation which not only yields accurate ionization energies but also an accurate spectral density. In this section we delineate a scheme for obtaining the Feynman-Dyson amplitudes and ionization energies from the 2p-h TDA propagator. The ionization energies so obtained are compared to those obtained from other approximations. In the next chapter, we present expressions relating the overlap amplitudes to ionization cross-sections. The calculated photoionization intensities will then be used for further comparison of the full 2p-h TDA with other approximations.

To extract the Feynman-Dyson amplitudes, following Purvis and Öhrn (1974) we recast the Dyson equation (1.5) as the operator equation

$$G^{-1}(E) = E - L(E) \qquad (1.31)$$

or equivalently,

$$(E-L(E))G(E) = I \qquad (1.32)$$

A formal solution of this equation can be expressed in terms of the biorthogonal expansion (Layzer, 1963) as

$$G(E) = \sum_n \frac{\Phi_n(E)\Phi_n^*(E)}{E-W_n(E)} \qquad (1.33)$$

where Φ_n and $W_n(E)$ are the solutions of the eigenvalue equation

$$L(E)\Phi_n(E) = W_n(E)\Phi_n(E) \qquad (1.34)$$

The solution of this equation in a discrete basis may be related to the overlap amplitudes from elementary residue calculus as

$$\lim_{E\to E_s} (E-E_s)G(E) = \ell_s\ell_s^* = \Gamma_s\Phi_s(E_s)\Phi_s^*(E_s) \qquad (1.35)$$

with

$$\Gamma_s^{-1} = \left[1-\frac{dW_s(E)}{dE}\right]_{E=E_s} \qquad (1.36)$$

and ℓ_s's denote either the f or g amplitudes (Eq. 1.27 and 1.28). A comparison of Eq. 1.26 and 1.33 reveals that the ionization energies are solutions of the equation

$$E = W_n(E) \qquad (1.37)$$

Table I. Full 2p-h TDA Ionization Energies for N_2

Orbital	Σ^a	Σ^b	Σ^c	Σ^{full}	$\Sigma^{diag.}$	I.P.(exp.)[d]
	44.50	43.07	43.0	41.77		
		41.90	41.78			
$2\sigma_g$	38.89	41.08	40.76	40.76	39.3	37.3
		38.58	38.39	38.38		
	29.25	29.23	29.17	29.17		
		37.13	36.84	36.84		
$2\sigma_u$	24.70	24.61	24.59	24.59		
	17.22	17.11	17.13	17.13	18.6	18.6
$1\pi_u$	17.06	17.26	17.21	17.21	17.4	16.8
$3\sigma_g$	13.92	14.25	14.2	14.2	15.1	15.5

a The two deepest core and the four highest virtuals with orbital energies differing by 1.0 H and more from the valence region (-1.70 H - 0.0 H) were dropped in the solution of Eq. 1.24.

b The two deepest core and the three highest virtuals with orbital energies differing by 1.50 H and more from the valence region were dropped.

c The two deepest core and the two highest virtuals with orbital energies differing by 2.0 H and more from the valence region were dropped.

d Purvis and Öhrn, 1975.

The equations 1.24, 1.35 and 1.37 were solved for N_2, H_2O and CN^- by modifying the GRNFNC program (Purvis, 1973; Born, 1979). One- and two-electron integrals over the contracted gaussian type orbitals were generated using MOLECULE (Almlöf, 1974).

The calculated and experimental ionization energies using Dunning's (1970) [9s, 5p/4s, 2p] basis set for N_2 are presented in Table I. This basis set is comparable to that employed by Schirmer et al. (1977), and our results do not differ in any significant manner. Surprisingly, while the diagonal approximation gives the correct ordering of $2\sigma_u$ and $1\pi_u$ ionization energies, the full 2p-h TDA ordering is marginally in error. The full 2p-h TDA calculations reveal a complete breakdown of the orbital picture for the $2\sigma_g$ orbital. In calculations with various subsets of orbitals, we find that the smallest subset gives results which correct the wrong ordering of $2\sigma_u$, $1\pi_u$ ionization energies. This uncertain quality of getting plausible results in good agreement with the experimental values with a small subset of molecular orbitals underscores the need for performing such calculations with successively larger subsets until a saturation is apparent. In the present calculation, such a saturation was achieved by including all the orbitals with orbital energies within 2.0 H of the region of interest (-1.70 - 0.0 H).

The results from the calculations on the H_2O molecule with 14 CGTO's and 26 CGTO's are presented in Tables II and III. The 14 CGTO basis set (Kurtz and Öhrn, 1979) is found to lack flexibility and obliterates the correlation effects which should lead to the breakdown of the orbital picture of ionization for the inner valence $2a_1$ orbital as shown by the calculations with the 26 CGTO basis set (Kurtz and Öhrn, 1978). The basis set dependence is typified by the $1b_1$ principal pole's shifting nearly 2 electron volts, from 13.1 ev with 14 CGTO's to 11.3 ev with

Table II. Full 2p-h TDA Ionization Energies for H_2O (14 CGTO)

Orbital	Σ^{full}	$\Sigma^{diag.}$	I.P.(exp.)[a]
$2a_1$	36.4 32.7	34.3	32.2
$3a_1$	14.8	13.2	14.7
$1b_2$	18.9	18.2	18.6
$1b_1$	13.1	11.2	12.6

[a] Siegbahn et al. (1969).

Table III. Full 2p-h TDA Ionization Energies for H_2O (26 CGTO)

Orbital	Σ^a	Σ^b	Σ^c	Σ^d	Σ^{full}	$\Sigma^{diag.}$	I.P.(exp.)[e]
$2a_1$		38.12	38.02	37.88	37.7		
		34.07	34.05	33.96	33.8		
	33.98	33.08	32.83	32.54	32.4	33.4	32.2
	32.57	30.64	30.60	30.28	30.20		
$3a_1$	13.69	13.45	13.45	13.49	13.6	13.7	14.7
$1b_2$	17.67	17.89	17.92	18.03	18.1	18.2	18.6
$1b_1$	11.51	11.12	11.15	11.25	11.3	11.4	12.6

[a] The deepest core and sixteen highest virturals with orbital energies differing by 1.0 H and more from the valence region (-1.50 - 0.0 H) were dropped.

[b] The deepest core and thirteen highest virtuals with orbital energies differing by 1.50 H and more from the valence region were dropped.

[c] The deepest core and eleven highest virtuals with orbital energies differing by 2.0 H and more from the valence region were dropped.

[d] The deepest core and six highest virtuals with orbital energies differing by 3.0 H and more from the valence region were dropped.

[e] Siegbahn et al. (1969).

26 CGTO's, while the corresponding change in the diagonal 2p-h TDA is only 0.2 eV. Once again, the results obtained by including only those orbitals with orbital energies within 1.0 H of the valence region (-1.05 H - 0.0 H) are misleading. Many calculations (Schirmer and Cederbaum, 1978b) have appeared in the literature, where all orbitals differing by more than 0.50 H from the valence region were dropped for convenience from the calculations. Our results indicate the need for further justification of such procedures.

Recently, Ortiz and Öhrn (1979) have used the self-energy approximant of Kurtz and Öhrn (1979) to calculate the electron affinity of CN^- as the ionization potential of the 5σ orbital. Their results indicate that the description of many-body effects is markedly sensitive to the quality of the computational basis set employed. To understand the effect of excluding orbitals obtained from large computational basis sets on the full 2p-h TDA calculations, we present in Table IV, the results obtained for the 5σ orbital by using their basis sets and excluding orbitals in the solution of Eq. 1.24. The fact that the smaller subset of the 46 CGTO MO's gives 5σ ionization potential in better agreement with the experimental value illustrates the care that one must take in quantitative comparisons when limited orbital basis sets are used.

Since ionizations from inner valence orbitals involve pronounced relaxation and intricate correlation, it should be no surprise that the diagonal approximations are unable to unveil a complex process like breakdown of the orbital picture of ionization for inner valence orbitals. Non-diagonal approximations like the full 2p-h TDA provide for the mixing of many more configurations and should be more efficacious. The results obtained confirm this hypothesis and caution against the spurious results which may surface if the choice of orbital basis set is not balanced

Table IV. Full 2p-h TDA Ionization Energy for 5σ Orbital in CN^-

	Full 2p-h TDA Ionization Potential					$\Delta SCF + \Sigma_{ii}^{Diag.\ TDA}$		
Orbital	34 CGTO[a]	34 CGTO[b]	34 CGTO[c†]	46 CGTO[d]	46 CGTO[e†]	34 CGTO[f]	46 CGTO[f]	I.P.(exp.)[g]
5σ	2.87	2.82	2.84	3.22	2.79	2.8	3.4	3.8

[a] The two deepest core and fifteen highest virtuals with orbital energies differing by 1.0 H or more from the valence region (-1.50 - 0.0 H) were dropped.

[b] The two deepest core and thirteen highest virtuals with orbital energies differing by 1.50 H or more were dropped.

[c] The two deepest core and ten highest virtuals with orbital energies differing by 2.0 H and more were dropped.

[d] The two deepest core and twenty-five highest virtuals with orbital energies differing by 1.0 H and more were dropped.

[e] The two deepest core and twenty-two highest virtuals with orbital energies differing by 1.50 H and more were dropped.

[f] Ortiz and Öhrn (1980).

[g] Berkowitz et al. (1969).

[†] Further saturation of the orbital basis set was not attempted, since inclusion of more than twenty-five orbitals in the full 2p-h TDA calculations is not feasible with the present facilities.

appropriately. The super-operator formulation for the use of symmetry adapted linear combination of creation and annihilation operators to block-diagonalize the super-operator resolvent matrix promises considerable savings in the implementation of all propagator approximations. The use of successively larger subsets in the full 2p-h TDA calculations not only provides a criterion for the reliability of these results but reveals a clear pattern in the apportioning of intensities between the different lines into which the principal peak of the orbital picture is split and as such provides a sound scheme for labelling the peaks of the photoelectron spectrum. The necessary formalism and calculations are described in the next chapter.

CHAPTER 2

USE OF PROPAGATOR AMPLITUDES IN THE CALCULATION OF PHOTOIONIZATION CROSS-SECTIONS

2.1 Introduction

The role played by Einstein's interpretation of photoelectric effect in the understanding of atomic and molecular structure is well known. Since then, photoelectron spectroscopy, which involves an analysis of the kinetic energy of electrons ejected from a system by an incident monochromatic beam of photons, has provided most suggestive and convincing evidence for the orbital picture of atoms and molecules (and also its breakdown in the most naive form). A typical photoelectron spectrum consists of a series of bands. If an orbital description of the electronic structure of atoms and molecules is assumed, the first band, corresponding to the highest observed kinetic energy, is associated with ionization from highest occupied orbital, having the lowest ionization potential. Successive bands then correspond to ionizations from successively lower lying orbitals, the spectrum terminating when there are no further levels from which electrons can be ejected by the fixed energy incident photons. With the advent of high resolution electrostatic kinetic energy analyzers the photoelectron spectrum reveals a rich structure of satellite peaks. These additional peaks arise primarily from "two-electron processes" involving the ionization of one electron accompanied by excitation of a second electron and provide important information about electronic correlation.

A scheme for understanding the involved energetics was presented in the previous chapter. However, the real power of photoelectron spectroscopy as an analytical tool for the investigation of atomic and molecular structure lies in the details of the principal and shake-up spectral bands. The shapes of these bands are related to photoionization cross-sections and serve as fingerprints for atoms and molecules. Comparison of experimental photoionization intensities with calculated cross-sections constitutes an important assignment aid in photoelectron spectroscopy. Especially important is the variation of relative intensities as a function of the incident photon energy which makes possible the observation of peaks absent for some sources, e.g., the $3\sigma_g$ peak in acetylene (Cavell and Allison, 1978). It is obvious that no treatment of bound-continuum transitions would be complete without a concomitant theoretical scheme for the calculation of photoionization cross-sections.

Extensive theoretical studies of atomic photoionization cross-sections are available (Bethe and Salpeter, 1977; Marr, 1967; McGinn, 1970; Huang and Ellison, 1974a). Calculations with varying degrees of approximation for small diatomics (Bates et al., 1953; Cohen and Fano, 1966; Flannery and Öpik, 1965; Kelly, 1973; Schneider and Berry, 1969; Tuckwell, 1970) and for several hydrocarbons (Johnson and Rice, 1968; Kaplan and Markin, 1968a, 1968b; Lohr and Robin, 1970) have appeared in the literature. Calculations using uncorrelated descriptions of the initial and final states in the CNDO, MS-Xα and HF approximations for the initial state and plane wave (Kaplan and Markin, 1968a, 1968b; Thiel and Schweig, 1971, 1972; Rabalais et al., 1974, 1975) or orthogonalized plane wave (Cavell and Allison, 1978; Allison and Cavell, 1978; Lohr, 1972; Rabalais et al., 1974, 1975; Huang and Ellison, 1974b) approximation to the ejected electron have been performed. Erudite discussion of the theoretical methodology and physical insights gained from these methods have been presented by several authors (Huang and Rabalais, 1978; Lohr, 1972; Kaplan and Markin, 1968a, 1968b; Schweig and Thiel, 1974; Ellison, 1974, 1975; Shirley, 1978). Encouraging results have been obtained with correlated treatments of ionization cross-sections using a plane-wave approximation for the ejected electron (Purvis and Öhrn, 1975; Herman et al., 1978; Born and Öhrn, 1979; Mishra and Öhrn, 1980a).

The plane wave approximation is inadequate for describing ionization processes involving substantial interaction between the photoelectron and the ionized target. It also gives an incorrect angular distribution for ionization intensities. The uncorrelated treatment is, of course, unsuitable for describing ionization processes involving considerable configuration interaction.

Recently many authors have communicated results which show a complete breakdown of the orbital picture of ionization for inner valence orbitals (Schirmer et al., 1977; Schirmer and Cederbaum, 1978b; Cederbaum et al., 1978; Mishra and Öhrn, 1980a). The sensitivity of the relative peak intensities to the correlation effects has been pointed out by recent publications (Herman et al., 1978; Martin and Shirley, 1976; Martin et al., 1976).

These considerations have prompted us to put forth a correlated treatment using propagator amplitudes to describe the ionization processes and the orthogonalized plane wave (OPW) approximation for the ejected electron. The Feynman-Dyson amplitudes of the electron propagator incorporate the correlation effects in ionization processes and lend themselves to systematic improvement (Öhrn, 1976; Cederbaum and Domcke, 1977; McCurdy et al., 1977). The OPW approximation provides for the necessary distortion of the plane wave, gives the correct form for the angular distribution, and ensures the orthogonality of the initial and the final N-particle states.

In the following sections we present the necessary formalism followed by the use of calculated intensities for further investigation of the full 2p-h Tamm Dancoff Approximation to the electron propagator.

2.2 Theory

The differential cross-section for bound-free transitions induced by incident radiation of angular frequency ω, direction of incidence $\vec{k}_\omega$ and polarization vector $\hat{n}$, into any number of free states with momentum $p = \hbar k$ in the solid angle $d\Omega$ about $\vec{k}$, using first order time-dependent perturbation theory and a semi-classical description of the radiation-matter interaction is given by (Schiff, 1968; Smith, 1971).

$$\frac{d\sigma_s(\vec{k},\vec{k}_\omega,\hat{n})}{d\Omega} = \frac{e^2L^3k}{2\pi mc\omega} |\langle N,s| \sum_j e^{i\vec{k}_\omega\cdot\vec{r}_j} \hat{n}\cdot\vec{\nabla}_j |N\rangle|^2 \tag{2.1}$$

where L is the edge length of a very large but finite cubic box used to normalize the continuum functions.

We choose the many electron ground state wave function of a closed shell system as

$$|N\rangle = \Psi_0(x_1,x_2,\ldots x_N) \tag{2.2}$$

with $x = (\vec{r},\zeta)$ a compound space-spin variable, and the final state $|N,s\rangle$ is represented by

$$\begin{aligned} |N,s\rangle = \left(\frac{N}{2}\right)^{\frac{1}{2}} O_{AS}[&v(\vec{k},\vec{r})\alpha(\zeta)\Psi_{s\beta}(x_1,x_2,\ldots x_{N-1}) \\ &- v(\vec{k},\vec{r})\beta(\zeta)\Psi_{s\alpha}(x_1,x_2,\ldots x_{N-1})] \end{aligned} \tag{2.3}$$

Here $\Psi_{s\alpha}$ and $\Psi_{s\beta}$ are the two doublet spin components of the (N-1)-electron ion, $v(\vec{k},\vec{r})$ denotes the wavefunction of the photoelectron, and the antisymmetrizer is

$$O_{AS} = N^{-1}[1-\sum_{i=1}^{N-1} P_{iN}] = O_{AS}^{+} \tag{2.4}$$

Where P_{iN} is the permutation operator which interchanges electron labels i and N. The form of Eq. 2.3 preserves the singlet spin symmetry of the system. Note that the antisymmetric wave functions Ψ_0 and Ψ_s are exact.

These choices for $|N>$ and $|N,s>$ lead to (Purvis and Öhrn, 1975)

$$\begin{aligned}<N,s|\sum_j e^{i\vec{k}_\omega\cdot\vec{r}_j}\hat{n}\cdot\vec{\nabla}_j|N> &= \sqrt{2}\int v^*(\vec{k},\vec{r})\exp(i\vec{k}_\omega\cdot\vec{r})\hat{n}\cdot\vec{\nabla}g_s(\vec{r})d\vec{r} \\ &+ \sqrt{2}\int v^*(\vec{k},\vec{r})\vec{p}_s(\vec{r})d\vec{r}\end{aligned} \tag{2.5}$$

where

$$N^{-\frac{1}{2}}g_s(\vec{r})x(\zeta) = \int\Psi_s^*(x_1,\ldots x_{N-1})\Psi_0(x_1,\ldots x_{N-1};\vec{r},\zeta)dx_1\ldots dx_{N-1} \tag{2.6}$$

with $x(\zeta)$ chosen as $\alpha(\zeta)$ or $\beta(\zeta)$, and

$$\begin{aligned}N^{-\frac{1}{2}}\vec{p}_s(\vec{r})x(\zeta) &= (N-1)\int\Psi_s^*(x_1,\ldots x_{N-1})\exp(i\vec{k}_\omega\cdot\vec{r}) \\ &\times \hat{n}\cdot\vec{\nabla}_1\Psi_0(x_1,\ldots x_{N-1};\vec{r},\zeta)dx_1\ldots dx_{N-1}\end{aligned} \tag{2.7}$$

The first term in Eq. 2.5 relates the Feynman-Dyson amplitude $g_s(\vec{r})$ to the photoionization cross-section. When $v(\vec{k},\vec{r})$ is strongly orthogonal to Ψ_0 the second term in Eq. 2.5 vanishes. This is ensured by the choice

$$v(\vec{k},\vec{r}) = N_0[1 - \sum_\ell|\Phi_\ell(\vec{r}-\vec{R}_\ell)><\Phi_\ell(\vec{r}-\vec{R}_\ell)|]|\vec{k}> \tag{2.8}$$

where

$$|\vec{k}> \;=\; L^{-3/2}\exp(i\vec{k}\cdot\vec{r}) \qquad (2.9)$$

and $\Phi_\ell(\vec{r}-\vec{R}_\ell)$ is the ℓth CGTO in the computational basis set, centered at position $\vec{R}_\ell$ in the molecular co-ordinate system. For the sake of clarity we would like to point out that ℓ labels the CGTO's, and $\vec{R}_\ell$ and $\vec{R}_m$ may be the same or different, depending on the case. This orthogonalization unifies the OPW and the extended OPW formulations.

It follows that the normalization constant N_0 is given by

$$N_0{}^2 \;=\; \{1 - 2L^{-3}\sum_\ell|<\ell|\vec{k}>|^2 + L^{-3}\sum_{\ell m}\sum<\ell|\vec{k}><\vec{k}|m><\ell|m>\}^{-1} \qquad (2.10)$$

which is taken to be unity for a very large box.

These considerations reduce Eq. 2.1 to the following form

$$\frac{d\sigma_s(\vec{k},\vec{k}_\omega,\hat{n})}{d\Omega} \;=\; \frac{e^2L^3k}{\pi mc\omega}|\hat{n}\cdot\vec{p}\,'|^2 \qquad (2.11)$$

where

$$\vec{p}\,' \;=\; \int v^*(\vec{k},\vec{r})\exp(i\vec{k}_\omega\cdot\vec{r})\vec{\nabla}g_s(\vec{r})d\vec{r} \qquad (2.12)$$

Now

$$v^*(\vec{k},\vec{r})\exp(i\vec{k}_\omega\cdot r) \;=\; L^{-3/2}[1 - \sum_\ell|\Phi_\ell><\Phi_\ell|]e^{-i(\vec{k}-\vec{k}_\omega)\cdot\vec{r}} \qquad (2.13)$$

Retaining $e^{i\vec{k}_\omega\cdot\vec{r}}$, thus, is tantamount to an effective retardation of the photoelectron. In the following equations we neglect this retardation, i.e., $\vec{k}-\vec{k}_\omega \simeq \vec{k}$ (the dipole approximation), whereby

$$\frac{d\sigma_s(\vec{k},\vec{k}_\omega,\hat{n})}{d\Omega} = \frac{e^2L^3k}{\pi mc\omega}|\hat{n}\cdot\vec{p}|^2 \tag{2.14}$$

where

$$\vec{p} = \int v^*(\vec{k},\vec{r})\vec{\nabla}g_s(\vec{r})d\vec{r} \tag{2.15}$$

The Feynman-Dyson amplitudes $g_s(\vec{r})$ are obtained from electron propagator calculations as a linear combination of some orbital basis (Purvis and Öhrn, 1974) (e.g., the HF basis in our work) which in turn can be expressed as a linear combination of computational CGTO basis. Hence, the amplitudes may be written as

$$g_s(\vec{r}) = \sum_{\ell} c_{\ell}^{s}\Phi_{\ell}(\vec{r}-\vec{R}_{\ell}) \tag{2.16}$$

The above expression for the differential cross-section, Eq. 2.14, describes the ionization for a particular $\vec{k}_\omega$ and a particular $\hat{n}$ in a specific photoelectron direction, $\vec{k}_f$. For comparison with spherical grid deflection-type measurements (Frost et al., 1968), done with unpolarized light and a gaseous sample of randomly oriented molecules, we must average over all $\hat{k}_\omega$, $\hat{n}$, and $\vec{k}_f$. First we present an expression for total cross-section (σ) suitable for comparison with spherical grid deflection-type measurements to be followed by a more general formulation to obtain differential cross-sections for a particular collection angle (e.g. $\sigma_\perp$).

We first average over all $\vec{n}$ and $\hat{k}_\omega$ (Doughty, 1964)

$$\frac{d\sigma_s(\vec{k})}{d\Omega} = \frac{e^2L^3k}{\pi mc\omega}\frac{1}{4\pi}\int d\hat{k}_\omega \tfrac{1}{2}\{|\hat{n}_1\cdot\vec{p}|^2 + |\hat{n}_2\cdot\vec{p}|^2\} \tag{2.17}$$

where $\hat{n}_1$ and $\hat{n}_2$ are two polarization directions normal to $\hat{k}_\omega$. Since $\hat{n}_1$,

$\hat{n}_2$ and $\hat{k}_\omega$ form a unit triad of vectors,

$$|\vec{p}|^2 = |\hat{n}_1\cdot\vec{p}|^2 + |\hat{n}_2\cdot\vec{p}|^2 + |\hat{k}_\omega\cdot\vec{p}|^2 \qquad (2.18)$$

$$\frac{d\sigma_s(\vec{k})}{d\Omega} = \frac{e^2L^3k}{8\pi^2mc\omega}\int d\hat{k}_\omega\{|\vec{p}|^2 - |\hat{k}_\omega\cdot\vec{p}|^2\} \qquad (2.19)$$

$$= \frac{e^2L^3k}{8\pi^2mc}|\vec{p}|^2\int d\hat{k}_\omega\{1 - |\hat{k}_\omega\cdot\hat{p}|^2\} \qquad (2.20)$$

This integral may be evaluated by taking $\hat{p}$ as an axis of a set of polar co-ordinates with $\hat{k}_\omega$ as the radial vector, and so

$$\frac{1}{8\pi}\int d\hat{k}_\omega(1 - |\hat{k}_\omega\cdot\hat{p}|^2) = \frac{1}{8\pi}\int d\hat{k}_\omega(1 - \cos^2\theta) = \frac{1}{3} \qquad (2.21)$$

which finally yields

$$\frac{d\sigma_s(\vec{k})}{d\Omega} = \frac{e^2L^3k}{3\pi mc\omega}|\vec{p}|^2 \qquad (2.22)$$

To evaluate $|\vec{p}|^2$ we define (Kaijser and Smith, 1977)

$$\xi_\ell(\vec{k}) = (2\pi)^{-3/2}\int e^{-i\vec{k}\cdot\vec{r}}\,\Phi_\ell(\vec{r})d\vec{r} \qquad (2.23)$$

whereby

$$\vec{p} = \sum_\ell [i\vec{k}c_\ell^S - \vec{m}_\ell]\exp(-i\vec{k}\cdot\vec{R}_\ell)\xi_\ell(\vec{k})L^{-3/2}(2\pi)^{3/2} \qquad (2.24)$$

and

$$\vec{m}_\ell = \sum_n c_n^S<\Phi_\ell(\vec{r}-\vec{R}_\ell)|\vec{\nabla}|\Phi_n(\vec{r}-\vec{R}_n) \qquad (2.25)$$

Substituting Eq. 2.24 into Eq. 2.22 yields

$$\frac{d\sigma_s(\vec{k})}{d\Omega} = \frac{8\pi^2 e^2 k}{3mc\omega}\{\sum_p \sum_q [k^2 c_p^s c_q^s + \vec{m}_p \cdot \vec{m}_q] \exp(-i\vec{k}\cdot\vec{R}_{pq})$$

$$\times\ \xi_p(\vec{k})\xi_q(\vec{k}) - 2\mathrm{Im}\sum_p \sum_q \vec{m}_p \cdot \vec{k} c_q^s \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^*(\vec{k})\} \tag{2.26}$$

where

$$\vec{R}_{pq} = \vec{R}_p - \vec{R}_q \tag{2.27}$$

Averaging Eq. 2.26 over all photoelectron directions yields

$$\sigma_s = \frac{8\pi^2 e^2 k}{3mc\omega}\{\sum_p \sum_q [k^2 c_p^s c_q^s + \vec{m}_p \cdot \vec{m}_q] \int \exp(-i\vec{k}\cdot\vec{R}_{pq})$$

$$\times\ \xi_p(\vec{k})\xi_q^*(\vec{k})d\Omega - 2\mathrm{Im}\sum_p \sum_q |\vec{m}_p||\vec{k}|$$

$$\times \int \cos\theta_{\vec{m}_p,\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^*(\vec{k})\Omega\} \tag{2.28}$$

which is suitable for comparison with experimental cross-sections measured in spherical grid deflection-type spectrometers.

The evaluation of the integrals

$$\int \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^*(\vec{k})d\Omega$$

and

$$\int \cos\theta_{\vec{m}_p,\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q(\vec{k})d\Omega$$

is detailed in the Appendix (A.21 and A.22).

Our treatment of differential cross-sections for a particular collection angle is closely patterned after the analysis of Ellison

(1974, 1975). As such, only skeletal derivations are provided which may easily be fleshed using identities in the Appendix. The rotation of real spherical harmonics being cumbersome, the treatment here is in terms of complex spherical harmonics for notational compactness. The phase conventions are due to Edmonds (1974) and our treatment of the overlap between the plane wave, and the Cartesian Gaussians is in terms of appropriate gaussians in the k-space (Kaijser and Smith, 1977) as opposed to the confluent hypergeometric functions (Ellison, 1974, 1975).

We define the laboratory co-ordinate system (x,y,z) and a molecular co-ordinate system (x',y',z'), their relative orientation being specified by the Euler Angles $\underline{B} = (\alpha,\beta,\gamma)$. Spherical harmonics $Y_{\ell m}(\theta',\phi')$ of the molecular co-ordinate system are related to those in the lab system by

$$Y_{\ell m'}(\theta',\phi) = \sum_{m=-\ell}^{\ell} D^{\ell}_{m,m'}(\underline{B})Y_{\ell,m}(\theta,\phi) \tag{2.29}$$

and, conversely,

$$Y_{\ell m}(\theta,\phi) = \sum_{m=-\ell}^{\ell} D^{\ell *}_{m,m'}(\underline{B})Y_{\ell,m'}(\theta',\phi') \tag{2.30}$$

where $D^{\ell}_{m,m'}(\underline{B})$ are elements of the usual rotation matrix (Edmonds, 1974). Other relevant identities are tabulated in the Appendix. The exciting radiation is assumed to be directed along the y-axis with its unit polarization vector $\hat{n}$ along the z-axis, and the propagation vector for the photoelectron is $\vec{k}$.

From Eq. 2.24

$$\hat{n}\cdot\vec{p} = \sum_{\ell} [ik\cos\theta_k c^s_{\ell} - \gamma_{\ell}]\exp(-i\vec{k}\cdot\vec{R}_{\ell})\xi_{\ell}(\vec{k})L^{-3/2}(2\pi)^{3/2} \tag{2.31}$$

where

$$\gamma_\ell = \sum_m \hat{n}\cdot\vec{\Delta}_{\ell m} c_m^S , \qquad \vec{\Delta}_{\ell m} = \langle \Phi_\ell | \vec{\nabla} | \Phi_m \rangle \tag{2.32}$$

$$= \sum_m \Delta_{\ell m} \cos\theta_m c_m^S \tag{2.33}$$

$$= \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \sum_m \Delta_{\ell m} Y_{10}(\theta_m,\phi_m) c_m^S \tag{2.34}$$

$$= \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \sum_n \sum_{m'=-1}^{1} \Delta_{\ell n} c_n^S D^{1*}_{0,m'}(\underline{B}) Y_{1m'}(\theta_n',\phi_n') \tag{2.35}$$

where

$$\theta_n' = \cos^{-1}\left(\frac{\Delta_{\ell n}^{z'}}{\Delta_{\ell n}}\right) \tag{2.36}$$

and

$$\phi_n' = \tan^{-1}\left(\frac{\Delta_{\ell n}^{y'}}{\Delta_{\ell n}^{x'}}\right) \tag{2.37}$$

or, from Eq. 2.14,

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{e^2L^3k}{\pi mc\omega}|\hat{n}\cdot\hat{p}|^2 \\ &= \frac{8\pi^2e^2k}{3mc\omega}\Big\{ \sum_p \sum_q [k^2\cos^2\theta_k c_p^S c_q^S + \gamma_p\gamma_q]\exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^*(\vec{k}) \\ &\quad - 2\,k\cos\theta_k \sum_p \sum_q \mathrm{Im}[c_q^S\gamma_p\exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^*(\vec{k})]]\Big\} \end{aligned} \tag{2.38}$$

This expression provides differential cross-section for a molecule with its orientation fixed by the Euler angles $\underline{B} = (\alpha,\beta,\gamma)$ relative to the laboratory co-ordinate system. For randomly oriented molecules we need to average Eq. 2.38 over all $\underline{B}$. Furthermore, for unpolarized light, an average over all polarization angles is appropriate.

The explicit dependence on $\underline{B}$ is displayed by the γ's, $\xi(\vec{k})$'s, and $\exp(-i\vec{k}\cdot\vec{R}_{pq})$, so we need to treat the following:

$$\int \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^*(\vec{k})d\underline{B} \quad / \quad \int d\underline{B} = Q_{pq} \tag{2.39}$$

$$\int \gamma_p\gamma_q\exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q(\vec{k})d\underline{B} \ / \int d\underline{B} = \Gamma_{pq} \tag{2.40}$$

$$\int \gamma_p\exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q(\vec{k})d\underline{B} \quad / \quad \int d\underline{B} = \chi'_{pq} \tag{2.41}$$

In the evaluation of Q_{pq} two cases arise. The first case is when $R_{pq} = 0$. In this case, using Appendix A. 20 and Eq. 2.29,

$$\xi_p(\vec{k})\xi_q^*(\vec{k}) = F_p(k)F_q^*(k) \sum_i \sum_j \sum_{L=|\ell_i-\ell_j|}^{\ell_i+\ell_j} c_i^p c_j^{q*} C_{L\ell_i\ell_j}^{Mm_im_j} \sum_{n=-L}^{L} D_{n,M}^{L}(\underline{B})Y_{L,n}(\theta_k,\phi k) \tag{2.42}$$

multiplying by $D_{00}^{0*}(\underline{B}) = 1$ and integrating over $\underline{B}$, using Appendix A.15 and A.16,

$$Q_{pq} = F_p^*(k)F_q(k) \sum_i \sum_j c_i^p c_j^{q*} C_{0\ell_i\ell_j}^{0m_im_j} Y_{00}(\theta_k,\phi_k) \tag{2.43}$$

$$= (4\pi)^{-\frac{1}{2}} F_p(k)F_q^*(k) \sum_i \sum_j c_i^p c_j^{q*} C_{0\ell_i\ell_j}^{0m_im_j} \tag{2.44}$$

In the second case $R_{pq} \neq 0$. In this case, using Appendix A.2 and A.20,

$$\exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^*(\vec{k}) = F_p^*(k) \sum_{i,j} \sum_{L} \sum_{\ell=0}^{\infty} \sum_{\ell'=|L-\ell|}^{L+\ell} \sum_{m=-\ell}^{\ell} (-i)^{\ell}$$

$$\times\ j_{\ell}(kR_{pq})c_i^p c_j^{q*} C_{L\ell_i\ell_j}^{Mm_im_j} C_{\ell'L\ell}^{m'Mm} Y_{\ell m}^*(\theta'_{R_{pq}},\phi'_{R_{pq}})$$

$$\times \sum_{n=-\ell'}^{\ell'} D^{\ell}_{n,m'}(\underline{B})Y_{\ell' n}(\theta_k,\phi_k) \tag{2.45}$$

Multiplying Eq. 2.45 by $D^{0*}_{00} = 1$ and using Appendix A.15 and A.16 to average over all $\underline{B}$,

$$Q_{pq} = (4\pi)^{-\frac{1}{2}} F_p(k)F_q(k) \sum_i \sum_j \sum_L \sum_{m=-L}^{L} (-i)^L j_L(kR_{pq})c^p_i c^{q*}_j$$
$$\times C^{Mm_i m_j}_{L\ell_i\ell_j} C^{0Mm}_{0LL} Y^*_{Lm}(\theta'_{R_{pq}},\phi'_{R_{pq}}) \tag{2.46}$$

We note that from Eq. 2.35 and Appendix A.13 and A.14,

$$\gamma_p\gamma_q = \frac{4\pi}{3} \sum_n \sum_t \sum_{m'} \sum_{m''=-1} \Delta_{pn}\Delta_{qt}c^s_n c^s_t Y_{1m'}(\theta'_{np},\phi'_{np})$$
$$\times Y_{1m''}(\theta'_{tq},\phi'_{tq})(-)^{m'+m''} \sum_{j=0}^{2} C^{-m'-m''k}_{1\ \ 1\ \ j} C^{000}_{11j} D^j_{0,k}(\underline{B})$$
$$k = -(m'+m'') \tag{2.47}$$

Also, from Eq. 2.35 and Appendix A.20,

$$\gamma_p\xi_p(\vec{k})\xi_q(\vec{k}) = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} F_p(k)F^*_q(k) \sum_n \sum_i \sum_j \sum_L c^p_i c^{q*}_j \Delta_{pn}c^s_n C^{Mm_i m_j}_{L\ell_i\ell_j}$$
$$\times \sum_{n'=-L}^{L} \sum_{m'=-1}^{1} Y_{L,n'}(\theta_k,\phi_k)Y_{1m'}(\theta'_{np},\phi'_{np})$$
$$\times D^{1*}_{0,m'}(\underline{B})D^L_{n',m}(\underline{B}) \tag{2.48}$$

From Eq. 2.42 and 2.47,

$$\gamma_p\gamma_q\xi_p(\vec{k})\xi^*_q(\vec{k}) = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} F_p(k)F^*_q(k) \sum_n \sum_t \sum_i \sum_j \sum_L c^p_i c^{q*}_j \Delta_{pn}\Delta_{qt}c^s c^s C^{Mm_i m_j}_{L\ell_k\ell_j}$$

$$\times \sum_{n'=-L}^{L} \sum_{m'}^{1} \sum_{m''=-1} Y_{1m'}(\theta'_{np},\phi'_{np})\, Y_{1m''}(\theta'_{tq},\phi'_{tq})$$

$$\times Y_{L,n'}(\ _k,\ _k)(-)^{m'+m''} \sum_{j'=0}^{2} C^{-m'\,-m''\,k}_{1\quad 1\quad j'}\, C^{000}_{11j'}$$

$$\times D^{j'}_{0,k}(\underline{B})\, D^{L}_{n'M}(\underline{B}) \qquad k = -(m'+m'') \qquad (2.49)$$

Similarly,

$$\gamma_p \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi^*_q(\vec{k}) = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} F_p(k)F^*_q(k) \sum_n \sum_i \sum_j \sum_L \sum_{\ell=0}^{\infty} \sum_{\ell'=|\ell-L|}^{\ell+L}$$

$$\times \sum_{m=-\ell}^{\ell} \sum_{m''=-1}^{1} (-i)^{\ell} j_\ell(kR_{pq}) c^p_i c^{q*}_j$$

$$\times \Delta_{pn} c^s_n\, C^{Mm_i m_j}_{L\ell_i \ell_j}\, C^{m'Mm}_{\ell' L\ell}\, Y^*_{\ell m}(\theta'_{R_{pq}},\phi'_{R_{pq}})$$

$$\times Y_{1m''}(\theta'_{np},\phi'_{np}) \sum_{n'=-\ell'}^{\ell'} Y_{\ell' n'}(\theta_k,\phi_k)$$

$$\times D^{1*}_{0,m''}(\underline{B})\, D^{\ell'}_{n',m'}(\underline{B}) \qquad (2.50)$$

$$\gamma_p\gamma_q \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi^*_q(\vec{k}) = \left(\frac{4\pi}{3}\right) F_p(k)F^*_q(k) \sum_n \sum_t \sum_i \sum_j \sum_L \sum_{\ell'} \sum_{\ell=0}^{\infty}$$

$$\times \sum_{m=-\ell}^{\ell} (-i)^{\ell} j_\ell(kR_{pq}) \Delta_{pn}\Delta_{qt} c^s_n c^s_t c^p_i c^{q*}_j$$

$$\times C^{Mm_i m_j}_{L\ell_i \ell_j}\, C^{m'''Mm}_{\ell'\ L\ell}\, Y^*_{\ell m}(\theta'_{R_{pq}},\phi'_{R_{pq}})$$

$$\times \sum_{m'}^{1} \sum_{m''=-1} (-)^{m'+m''}$$

$$\times \sum_{j'=0}^{2} C^{-m'\,-m''\,-(m'+m'')}_{1\quad 1\quad j'}\, C^{000}_{11j'}$$

$$\times\, Y_{1m'}(\theta'_{np},\phi'_{np})\; Y_{1m}(\theta'_{tq},\phi'_{tq})$$

$$\times\, D^{j'}_{0,-m'-m''}(\underline{B})$$

$$\times \sum_{m'=-\ell'}^{\ell'} D^{\ell'}_{n',m'''}(\underline{B})\, Y_{\ell' n'}(\theta_k,\phi_k) \tag{2.51}$$

In the evaluation of Γ_{pq} two cases arise. The first case is when $R_{pq} = 0$. In this case, using Eq. 2.49 and Appendix A.14, A.15 and A.16, since

$$\frac{\int D^{L}_{n',m}(\underline{B})\, D^{j'}_{0,-m'-m''}(\underline{B})\, d\underline{B}}{\int d\underline{B}} = (-)^{m'+m''}(2j'+1)^{-1}\delta_{L,j'}$$

$$\times\, \delta_{M,-m'-m''}\,\delta_{n',0} \tag{2.52}$$

then

$$\Gamma_{pq} = \left(\frac{4\pi}{3}\right) F_p(k)F^*_q(k) \sum_n \sum_t \sum_i \sum_j \sum_{m',m''=-1}^{1} \sum_{j'=0}^{2} c^p_i c^{q*}_j\, \Delta_{pn} c^s_n c^s_t\, \Delta_{qt}$$

$$\times\, (2j'+1)^{-1}\, C^{k'm_i m_j}_{j'\ell_i\ell_j}\, Y_{j',0}(\theta_k,\phi_k)\, C^{-m'\,-m''\,-(m'+m'')}_{1\;\;1\;\;j'}\, C^{000}_{11j'}$$

$$\times\, Y_{1m'}(\theta'_{np},\phi'_{np})\, Y_{1m''}(\theta'_{tq},\sigma'_{tq}) \qquad k' = -(m'+m'') \tag{2.53}$$

In the second case, $R_{pq} \neq 0$. Using Eq. 2.51 and Appendix A.15 and A.16,

$$\Gamma_{pq} = \left(\frac{4\pi}{3}\right) F_p(k)F^*_q(k) \sum_n \sum_t \sum_i \sum_j \sum_{L=|\ell_i-\ell_j|}^{\ell_i+\ell_j} \sum_{\ell} \sum_{m=-\ell}^{\ell} (-i)^{\ell}\, j_{\ell}(kR_{pq})$$

$$\times\, \Delta_{pn}\Delta_{qt} c^s_n c^s_t c^p_i c^{q*}_j\, C^{Mm_i m_j}_{L\ell_i\ell_j}\, Y^*_{\ell m}(\theta'_{R_{pq}},\phi_{R_{pq}}) \sum_{j'=0}^{2} \sum_{m',m''=-1}^{1}$$

$$\times\, C^{k'Mm}_{j'L\ell}\, C^{-m'-m''k'}_{1\ \ 1\ \ j'}\, (2j'+1)^{-1}\, C^{000}_{11j'}\, Y_{1m'}(\theta'_{np},\phi'_{np})$$

$$\times\, Y_{1m}(\theta'_{tq},\phi'_{tq})\, Y_{j',0}(\theta_k,\phi_k) \qquad (2.54)$$

In the evaluation of χ'_{pq} two cases arise. The first case is when $R_{pq} = 0$. In this case, using Eq. 2.48 and Appendix A.15 and A.16,

$$\chi'_{pq} = \frac{1}{3}\left(\frac{4\pi}{3}\right)^{\frac{1}{2}} F_p(k)F^*_q(k) \sum_n \sum_i \sum_j \sum_{m'=-1}^{1} c^{q*}_j \Delta_{pn} c^s_n\, C^{m'm_i m_j}_{1\ \ell_i \ell_j}$$

$$\times\, Y_{10}(\theta_k,\phi_k)\, Y_{1m'}(\theta'_{np},\phi'_{np})$$

$$= \cos\theta_k \chi_{pq} \qquad (2.55)$$

In the second case, $R_{pq} \neq 0$. Using Eq. 2.50 and Appendix A.15 and A.16,

$$\chi'_{pq} = \frac{1}{3}\left(\frac{4\pi}{3}\right)^{\frac{1}{2}} F_p(k)F^*_q(k) \sum_n \sum_i \sum_j \sum_{L=|\ell_i-\ell_j|}^{\ell_i+\ell_j} \sum_{\ell} \sum_{m=-\ell}^{\ell} \sum_{m''=-1}^{1} \Delta_{pn}$$

$$\times\, c^s_n(-i)^{\ell}\, j_{\ell}(kR_{pq}) c^p_i c^{q*}_j\, C^{Mm_i m_j}_{L\ell_i\ell_j}\, C^{m''Mm}_{1\ L\ell}\, Y^*_{\ell m}(\theta'_{R_{pq}},\phi R'_{pq})$$

$$\times\, Y_{1m''}(\theta'_{np},\phi'_{np})\, Y_{10}(\theta_k,\phi_k)$$

$$= \cos\theta_k \phi_{pq} \qquad (2.56)$$

With these relationships, Eq. 2.38 for differential ionization cross-sections due to polarized light with polarization vector $\hat{n}$ incident on a gaseous sample of randomly oriented molecules may be written as

$$\frac{\overline{d\sigma}}{d\Omega} = \frac{8\pi^2 e^2 k}{3mc\omega} \{\sum_p \sum_q [k^2 \cos^2\theta_k Q_{pq} + \Gamma_{pq} - 2k\cos^2\theta_k \mathrm{Im}(\chi_{pq})]\} \qquad (2.57)$$

where Γ_{pq} provides the spherical contributions to the distribution of ejected electrons. It is well known that the angular dependence of the differential cross-sections is given by (Tully et al., 1968; Yang, 1948; Cooper and Zare, 1968; Buckingham et al., 1970; McGowan et al., 1969)

$$\frac{d\bar{\sigma}}{d\Omega} = \frac{\sigma}{4\pi}[1 + \beta P_2(\cos\theta_k)] \tag{2.58}$$

where β is the asymmetry parameter. Defining

$$\sigma_\perp = \left(\frac{d\bar{\sigma}}{d\Omega}\right)_{\theta_k=90^\circ} \tag{2.59}$$

and

$$\bar{\sigma}_\parallel = \left(\frac{d\bar{\sigma}}{d\Omega}\right)_{\theta_k=0^\circ} \tag{2.60}$$

from Eq. 2.59 and 2.60, we find

$$\sigma = \frac{4\pi(\bar{\sigma}_\parallel + \bar{\sigma}_\perp)}{3} \tag{2.61}$$

and

$$\beta = \frac{2(\bar{\sigma}_\parallel - \bar{\sigma}_\perp)}{(\bar{\sigma}_\parallel + 2\bar{\sigma}_\perp)} \tag{2.62}$$

For unpolarized light the angle θ_k between the polarization vector $\hat{n}$ and the propagation vector $\vec{k}$ cannot be specified uniquely. However, for any particular collection angle, e.g. 90° to the direction of incidence, the angle between $\vec{k}$ and the direction of incidence (y-axis) is automatically fixed. By defining a new polar co-ordinate system with the direction of incidence as the polar axis, using Appendix A.7, the $\cos\theta_k$

dependence can easily be reformulated. Finally averaging over all the polarization angles gives (Ellison, 1974, 1975)

$$\sigma_{\perp} = \frac{\sigma}{4\pi}(1 + \tfrac{1}{2}\beta) \qquad (2.63)$$

which is suitable for comparison with the cross-sections obtained in the most popular experimental setup.

The theory of molecular photoionization cross-sections lags far behind the experiments. The present formulation meets the necessary formal requirements. It treats principal and satellite peak intensities within a single theoretical and computational scheme and unifies the PW, OPW and the extended OPW approaches to the continuum wave functions. We have presented two different formulations to facilitate an easy implementation of this approach using the two widely different computational strategies (Thiel and Schweig, 1971, 1972; Rabalais et al., 1974, 1975; Cavell and Allison, 1978; Allison and Cavell, 1978). The use of single determinantal descriptions for Ψ_0^N and Ψ_s^{N-1} in Eq. 2.1 coupled with frozen orbital approximation leads to the OPW formulation of Ellison (1974, 1975), where the propagator amplitude in Eq. 2.12 is replaced by the corresponding orbital. As such, this derivation also provides an alternate computational scheme within the confines of HF approximation. Spherical grid and magic angle [54.74° for which $P_2(\cos\theta)$ vanishes] cross-section measurements may be used to check the first formulation. The $\sigma_{\perp}$ measurements can ascertain the importance of the second formulation.

2.3 The Use of Cross-section Calculations for Further Comparison of Full 2p-h TDA and Other Self-energy Approximants

Real merit of the scheme outlined in the previous section is in its unifying versatility. The plane wave (PW) approximation is recovered by retaining only first term in Eq. 2.28 and 2.57 (Ellison, 1974, 1975; Purvis and Öhrn, 1975). The correct angular distribution

$$I(\theta) \quad \alpha \quad \{1 + \frac{\beta}{2}(3\cos^2\theta - 1)\} \qquad (2.64)$$

given by the OPW approximation makes possible a study of variations in the angular asymmetry parameter β. The parameter β depends on incident ionizing radiation and the orbital(s) involved in the ionization process. Accurate calculation of β thus serves as a potent assignment aid in the interpretation of angularly resolved photoelectron spectra. The plane wave approximation leads to the angular distribution

$$I(\theta) \quad \alpha \quad \cos^2\theta \qquad (2.65)$$

which sets $\beta = 2$ for ionizations from all orbitals with different angular dependence and limits its utility. Use of propagator amplitudes permits the treatment of principal and satellite (correlation) peak intensities within the same scheme. Summing up, the procedure outlined above could make possible an interpretation and study of finer details of the photoelectron spectrum in a way unactuated before.

The use of OPW approximation has definite advantages. However, if finer details of the spectrum are not to be elicited from the theory and only relative intensities for ionizations by high energy radiation sources, [e.g., Mgk_α (~1254 ev)] are sought, the plane wave approximation may suffice. An inspection of Eq. 228 and 2.57 suggests that for high energy photoelectrons (large k), the PW contribution to total intensities will be dominant, and the OPW corrections could be neglected since the PW term is multiplied by k^3 while the OPW corrections are multiplied by k or k^2. The

Table V. Ionization Cross-sections and Potentials for N_2[†]

Orbital	Σ^a	Σ^b	Σ^c	Σ^{full}	$\Sigma^{diag.}$	I.P.(exp.)^d	σ^a	σ^b	σ^c	σ^{full}	$\sigma^{diag.}$	σ(exp.)^e
	44.50	43.07 41.90	43.0 41.78	41.77			0.323	0.0189 0.300	0.0018 0.394	0.388		
$2\sigma_g$	38.89	41.08 38.58	40.76 38.39	40.76 38.38	39.3	37.3	0.854	0.3467 0.446	0.310 0.387	0.388 0.392	1.20	0.70
	29.25	29.23	29.17	29.17			0.100	0.0847	0.087	0.087		
		37.13	36.84	36.84				0.0455	0.043	0.043		
$2\sigma_u$	24.70	24.61	24.59	24.59			0.060	0.0540	0.054	0.054		
	17.22	17.11	17.13	17.13	18.6	18.6	0.940	0.900	0.902	0.903	1.00	1.00
$1\pi_u$	17.06	17.26	17.21	17.21	17.4	16.8	0.088	0.0845	0.084	0.083	0.084	0.164
$3\sigma_g$	13.92	14.25	14.2	14.2	15.1	15.5	0.188	0.196	0.195	0.194	0.195	0.200

[†] For easy comparison with the Hartree Fock and the experimental results, we have normalized the relative intensities with respect to the sum of the cross-sections for all the satellite plus the principle poles for the $2\sigma_u$ ionization.

Table V - Continued

[a] The two deepest core and the four highest virtuals with orbital energies differing by 1.0 H and more from the valence region (-1.70 H - 0.0H) were dropped in the solution of Eq. 2.29.

[b] The two deepest core and the three highest virtuals with orbital energies differing by 1.50 H and more from the valence region were dropped.

[c] The two deepest core and the two highest virtuals with orbital energies differing by 2.0 H and more from the valence region were dropped.

[d] Purvis and Öhrn, 1974.

[e] Rabalais et al., 1974, 1975.

results of Rabalais et al. (1974, 1975) corroborate this observation. The PW approximation also has the advantage of computational ease.

The Feynman-Dyson amplitudes determine the ionization intensities. Calculated relative intensities using propagator amplitudes may thus serve as additional indicators of the efficacy of various self-energy approximants. In Tables V, VI and VII we present the calculated relative intensities corresponding to the ionization of N_2 and H_2O molecules by Mgk_α radiation source, using plane wave approximation for the photoelectron.

An examination of the relative intensities, calculated in the diagonal and the non-diagonal approximations, confirms the breakdown of the orbital picture of ionization for the inner valence orbitals; however, no significant difference is evidenced for the outer valence orbitals. An average of the calculated ionization potentials weighted by the corresponding cross-sections gives the values (ev) 32.5, 39.4, 18.4 for the H_2O $2a_1$, N_2 $2\sigma_g$ and $2\sigma_u$, respectively, in close agreement with the results obtained from the diagonal approximation and experiments. A careful examination of the results obtained from various subsets reveals a clear pattern in the apportioning of intensities between the different lines, into which the principal peak of the orbital picture is split. The use of intensities obtained from successively larger subsets thus provides a sound scheme for labelling the peaks of the photoelectron spectrum.

The relative intensities obtained from various subsets differ markedly. Stable results are obtained only when all orbitals within 3.0 H of the valence region (-1.50,-0.0 H) are retained for H_2O and within 2.0 H of the valence region (-1.70,-0.0 H) are included for N_2.

Table VI. Ionization Cross-Sections and Potentials for H_2O (14 CGTO)

Orbital	Σ^{full}	$\Sigma^{diag.}$	I.P.(exp.)[a]	σ^{full}	$\sigma^{diag.}$	σ(exp.)[b]
$2a_1$	36.4	34.3	32.2	0.996	1.000	1.00
	32.7			0.004		
$3a_1$	14.8	13.2	14.7	0.229	0.316	0.260
$1b_2$	18.9	18.2	18.6	0.095	0.109	0.085
$1b_1$	13.1	11.2	12.6	0.137	0.165	0.095

a Siegbahn et al., 1969.

b Rabalais et al., 1974, 1975.

Table VII. Ionization Cross-sections and Potentials for H_2O (26 CGTO)[†]

Orbital	Σ^a	Σ^b	Σ^c	Σ^d	Σ^{full}	$\Sigma^{diag.}$	I.P.(exp)[e]	σ^a	σ^b	σ^c	σ^d	σ^{full}	$\sigma^{diag.}$	σ(exp.)[f]
$2a_1$		38.12	38.02	37.88	37.7				0.116	0.103	0.099	0.095		
		34.07	34.05	33.96	33.8				0.049	0.0357	0.0196	0.017		
	33.98	33.08	32.83	32.54	32.4	33.4	32.2	0.711	0.702	0.700	0.660	0.690	1.00	1.00
	32.57	30.64	30.60	30.28	30.20			0.288	0.132	0.162	0.221	0.198		
$3a_1$	13.69	13.45	13.45	13.49	13.6	13.7	14.7	0.244	0.250	0.253	0.262	0.263	0.243	0.260
$1b_2$	17.67	17.89	17.92	18.03	18.1	18.2	18.6	0.0865	0.0887	0.0886	0.090	0.091	0.087	0.081
$1b_1$	11.51	11.12	11.15	11.25	11.3	11.4	12.6	0.137	0.134	0.134	0.136	0.137	0.134	0.095

[†] For comparison with the Hartree Fock and the experimental results (Siegbahn et al., 1969; Rabalais et al., 1974, 1975), the relative intensities have been normalized with respect to the sum of the cross-sections for all the satellite plus the principal poles for the $2a_1$ ionization.

[a] The deepest core and sixteen highest virtuals with orbital energies differing by 1.0 H and more from the valence region (-1.50 - 0.0 H) were dropped.

[b] The deepest core and thirteen highest virtuals with orbital energies differing by 1.50 H and more from the valence region were dropped.

[c] The deepest core and eleven highest virtuals with orbital energies differing by 2.0 H and more from the valence region were dropped.

Table VII - Continued

d The deepest core and six highest virtuals with orbital energies differing by 3.0 H and more from the valence region were dropped.

e Siegbahn et al., 1969.

f Rabalais et al., 1974, 1975.

It should be noted that the sole use of pole strengths as estimates for the relative ionization intensities in depicting a theoretical photoelectron spectrum (Cederbaum et al., 1978) is misleading. For instance the pole strength for the $1\pi_u$ pole of N_2 is 0.92 while the relative intensity is calculated to be 0.083.

CHAPTER 3

TREATMENT OF QUASI-BOUND CONTINUUM TRANSITIONS BY DILATION OF THE ELECTRON PROPAGATOR

3.1 Resonances

In elastic electron-atom or electron-molecule scattering, the following process may occur:

$$e + A \longrightarrow (A^-)^* \longrightarrow e + A \tag{3.1}$$

This involves a temporary trapping of the incident electron by the target A, which leads to severe distortion of the incident beam, causing a large phase shift in the scattered wave which manifests itself as a sharp increase of the scattering cross-section. These features characterize resonant scattering and define resonances as quasi-bound (meta-stable) anionic states $(A^-)^*$ which decay by electron emission (Schulz, 1973). The resonance energy, i.e., the kinetic energy of the incident beam for which resonances occur, is obtained from Eq. 3.1 as

$$E_R = K \cdot E_e = E_{(A^-)^*} - E_A \tag{3.2}$$

and is equal to the electron affinity of the excited target A*. This association of resonance energies with electron affinity immediately suggests the use of electron propagator formalism for their direct calculation in conjunction with a scheme which allows for the easy differentiation of these quasi-bound states from other states in the continuum part of the spectrum of the A^- Hamiltonian. Such a scheme is presented by the theorems of Aguilar, Balslev and Combes (Aguilar and Combes, 1971; Balslev and Combes, 1971; Simon, 1972). These theorems (to be referred as ABC Theorems) provide a beautiful characterization of the pole structure of the dilatated resolvent $(Z-H_\theta)^{-1}$. The dilatation transformation involves the replacement of $\vec{r}_i$ by $\vec{r}_i\exp(i\theta)$ $(0<\theta<\frac{\pi}{2})$ in the co-ordinate representation of the Hamiltonian. The Born-Oppenheimer molecular Hamiltonian is not dilatation analytic (Simon, 1978), and in the following discussions, we limit ourselves to atomic Hamiltonians. The ordinary N+1 electron atomic Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N+1} \nabla_i^2 - Z\sum_i \frac{1}{r_i} + \sum_{i<j}\frac{1}{r_{ij}} \tag{3.3}$$

on dilatation transformation $[\vec{r}_i \longrightarrow \vec{r}_i\exp(i\theta)]$ is transformed into

$$H(\theta) = -\frac{1}{2}e^{-2i\theta}\sum_i \nabla_i^2 - Ze^{-i\theta}\sum_i \frac{1}{r_i} + e^{-i\theta}\sum_{i<j}\frac{1}{r_{ij}} \tag{3.4}$$

The ABC theorems divide the eigenvalue spectrum of $H(\theta)$ into a discrete point spectrum $\sigma_d(\theta)$, a continuous essential spectrum $\sigma_e(\theta)$, and a set of complex thresholds $\sigma_t(\theta)$. The spectrum of $H(\theta)$ is composed of the following elements: a) A set of real points in $\sigma_d(\theta)$ and in $\sigma_t(\theta)$. The real elements in $\sigma_d(\theta)$ are the ordinary bound states of the (N+1)-electron system; those in $\sigma_t(\theta)$ are the real thresholds. These real elements in $\sigma_d(\theta)$ and $\sigma_t(\theta)$ are independent of θ. b) An essential spectrum $\sigma_e(\theta)$ which consists of a number of complex rays each making an angle -2θ to the positive real axis. Each ray begins at one of the real thresholds of H and may be regarded as a rotated branch cut. In addition to these, there also exists a set of rays which begin at the complex (resonance) thresholds in $\sigma_t(\theta)$. These latter also make an angle

-2θ to the positive real axis. c) A set of complex discrete eigenvalues in $\sigma_d(\theta)$ and $\sigma_t(\theta)$. These are defined to be resonances of the (N+1) electron system with $Z = E - i\frac{\Gamma}{2}$, where E and Γ are the energy and width of the resonance state, respectively. In the two-body case, the resonances so defined have been shown to be identical to the poles of the analytically continued scattering amplitude (Simon, 1973), imbuing this definition with some validity. In the general many-body case, the work of Sigal (1978) is promising. Each resonance eigenvalue lies on a sector or sheet of the complex plane bounded by two of the rays described in part b above. On a given sheet, the resonance eigenvalue is independent of θ.

These features make possible the description of quasi-bound continuum transitions within the electron propagator formalism. We consider the following eigenvalue equations for the number-free dilatated atomic Hamiltonians

$$H(\theta)|{}^{N}_{0}>_{\theta} = E^{N}_{0}|{}^{N}_{0}>_{\theta} \qquad H(\theta)|{}^{N\pm1}_{s}>_{\theta} = E^{N\pm1}_{s,\theta}|{}^{N\pm1}_{s}>_{\theta} \tag{3.5}$$

where the eigenvalue E^N_0 for the N-particle ground state $|{}^{N}_{0}>_{\theta}$ is independent of the rotation parameter θ (Aguilar and Combes, 1971; Balslev and Combes, 1971). The complex conjugate of these exact eigenfunctions will be the eigenfunctions of $H^{+}(\theta)$, and the following identity holds :

$$1^{N\pm1} = \sum_{n} |{}^{N\pm1}_{n}>_{\theta\theta}<\overline{{}^{N\pm1}_{n}}| \tag{3.6}$$

where the bar denotes complex conjugation. In terms of the dilatationally transformed Hamiltonian $H(\theta) \equiv H_\theta$, the time development of Heisenberg operators is described by the similarity transformation

$$A(t) = e^{iH_\theta t} A(0) e^{-iH_\theta t} \qquad A(0) \equiv A \tag{3.7}$$

The generalized equation of motion is

$$i\,\frac{\partial A(t)}{\partial t} = [A(t),H_\theta]_- \tag{3.8}$$

and $H_\theta(t) = H_\theta$ is maintained. We define the dilated electron propagator

$$\begin{aligned} G_{rs}(\theta,t,t') &= \langle\langle a_r(t)\ ;\ a_s^{+}(t')\rangle\rangle \\ &= -\,i\theta(t-t')\,{}_{\theta}\langle{}^{\overline{N}}_{0}|a_r(t)a_s^{+}(t')|{}^{N}_{0}\rangle_{\theta} \\ &\quad +\,i\theta(t'-t)\,{}_{\theta}\langle{}^{\overline{N}}_{0}|a_s^{+}(t')a_r(t)|{}^{N}_{0}\rangle_{\theta} \end{aligned} \tag{3.9}$$

where $\theta(t-t')$ is the Heaviside stepfunction.

In obvious analogy with the ordinary electron propagator theory (Linderberg and Öhrn, 1973), by using identities Eq. 3.6 and Eq. 3.7, the Fourier transform of Eq. 3.9 would provide the following spectral representation of the dilated electron propagator

$$\begin{aligned} G_{rs}(\theta,E) = \langle\langle a_r,a_s^{+}\rangle\rangle_E = \lim_{\eta\to o^{+}}\sum_n \Bigg[&\frac{{}_{\theta}\langle{}^{\overline{N}}_{0}|a_r|{}^{N+1}_{n}\rangle_{\theta\theta}\langle{}^{\overline{N+1}}_{n}|a_s^{+}|{}^{N}_{0}\rangle_{\theta}}{E-\{E_n^{\theta}(N+1)-E_0(N)\}+i\eta} \\ &+\frac{{}_{\theta}\langle{}^{\overline{N}}_{0}|a_s^{+}|{}^{N-1}_{n}\rangle_{\theta\theta}\langle{}^{\overline{N-1}}_{n}|a_r|{}^{N}_{0}\rangle_{\theta}}{E-\{E_0(N)-E_n^{\theta}(N-1)\}-i\eta}\Bigg] \end{aligned} \tag{3.10}$$

It is obvious that the pole structure of the dilated electron propagator would be similar to that of the dilated resolvents as described by the theorems of Aguilar, Balslev and Combes, except that the poles here correspond to energy differences between N and N±1 electron states (Winkler, 1977; Donnelly and Simons, 1980). Specifically, the dilated electron propagator will have isolated complex poles in sectors between the adjacent branch cuts, which once uncovered will be independent of θ.

These complex poles z correspond to

$$z = \left(E_{res}^{N+1} - E_0^N\right) - i\,\frac{\Gamma_{res}^{N+1}}{2} \tag{3.11}$$

since the stable target has zero width, and are to be associated with resonances. It follows that, by dilating the electron propagator, a computation performed on the neutral (N-particle) parent would yield the resonance energy and width of interest. The construction of such a propagator is the main concern of this chapter. The non-hermiticity of dilatated Hamiltonians necessitates some fundamental changes to the usual scheme for the construction of the electron propagator. In the next section we describe a bi-variational SCF procedure for dilatated Hamiltonians. The use of creation and annihilation operators defined on the bi-variationally obtained bi-orthonormal orbitals in the construction of the dilated electron propagator is described in the last section.

3.2 The Bi-variational SCF

The typical dilated atomic Hamiltonian (in a.u.)

$$H(\theta) = \sum_i \left(-\tfrac{1}{2}e^{-2\theta}\,\nabla_i^2 - e^{-\theta}\,\frac{Z}{r_i}\right) + \sum_{i<j} e^{-\theta}\,\frac{1}{r_{ij}} \tag{3.12}$$

is non-Hermitian for complex values of the dilation parameter θ, and, as such, the variational theorem does not apply. However, there exists a bi-variational theorem (Löwdin, 1978) for non-Hermitian operators. The bi-variational SCF-equations for the dilated Hamiltonians are derived by extremizing the generalized functional

$$\mathcal{E}(\Phi_0,\Psi_0) = \frac{\langle\Phi_0|H(\theta)|\Psi_0\rangle}{\langle\Phi_0|\Psi_0\rangle} \tag{3.13}$$

under the constraint that the solutions Φ_0 and Ψ_0 will be of determinantal type and that the constituent one-electron orbitals will be bi-orthogonal.

$$\Phi_0 = (N!)^{-\frac{1}{2}} \det\{\phi_1(x_1)\phi_2(x_2)\ldots\phi_N(x_N)\} \tag{3.14}$$

$$\Psi_0 = (N!)^{-\frac{1}{2}} \det\{\psi_1(x_1)\psi_2(x_2)\ldots\psi_N(x_N)\} \tag{3.15}$$

$$\langle\phi_i|\psi_j\rangle = \delta_{ij} \tag{3.16}$$

This has been shown (Froelich, 1980a) to result in a canonical bi-variational SCF procedure leading to the effective Fock operators

$$\Omega_1(\theta,\underline{\psi},\underline{\phi}) = -\tfrac{1}{2}e^{-2\theta}\,\nabla_1^2 - e^{-\theta}\frac{Z}{r_1} + \int_{x_2'=x_2} \frac{1-P_{12}}{r_{12}}\,\rho(x_2,x_2')dx_2 \tag{3.17}$$

and

$$\Omega_1^{+}(\theta,\underline{\psi},\underline{\phi}) = -\tfrac{1}{2}e^{-2\theta^*}\,\nabla_1^2 - e^{-\theta^*}\frac{Z}{r_1} + \int_{x_2'=x_2} \frac{1-P_{12}}{r_{12}}\,\rho^{+}(x_2,x_2')dx_2 \tag{3.18}$$

where

$$\rho = {}_{occ.}|\underline{\psi}\rangle\langle\underline{\phi}|_{occ.} \tag{3.19}$$

Extremization of the functional in Eq. 3.13 defines the necessary and sufficient condition (Löwdin, 1981)

$$\Omega\rho = \rho\Omega \tag{3.20}$$

and the following SCF equations result

$$\Omega\psi_i = \varepsilon_i\psi_i \tag{3.21}$$

$$\Omega^+\phi_i = \varepsilon_i^*\phi_i \tag{3.22}$$

The N lowest real orbital energies ε_i determine the occupied spin orbitals which define ρ, Ω, Ψ_0, Ω^+ and Φ_0.

The procedure followed uses a finite real basic set $\underline{u} = \{u_i\}_{i=1}^{M}$, M>N, such that

$$\underline{\bar{\psi}} = \underline{u}\underline{c} \qquad\qquad \underline{\bar{\phi}} = \underline{u}\underline{d} \tag{3.23}$$

(the bars on top of $\underline{\bar{\psi}}$ and $\underline{\bar{\phi}}$ denote their approximate nature), and by applying the bi-variational theorem again (Löwdin, 1981) to the functional

$$\eta = \frac{\langle\bar{\phi}|\Omega\bar{\psi}\rangle}{\langle\bar{\phi}|\bar{\psi}\rangle} \tag{3.24}$$

and its complex conjugate, we obtain the matrix equations

$$\underline{\Omega}\underline{c} = \underline{\Delta}\underline{c}\underline{\eta} \tag{3.25}$$

$$\underline{\Omega}^+\underline{d} = \underline{\Delta}\underline{d}\underline{\eta}^* \tag{3.26}$$

and the bi-orthoganality relation

$$\underline{d}^\dagger\underline{\Delta}\underline{c} = \underline{1} \tag{3.27}$$

where $\underline{\Delta} = \langle\underline{u}|\underline{u}\rangle$ is the real and symmetric matrix and $\underline{\Omega} = \langle\underline{u}|\Omega\underline{u}\rangle$ is symmetric but complex.

The fact that $H^+(\theta) = H(\theta^*) = H^*(\theta)$ suggests the assumption $\Phi_0 = \Psi_0^*$ and the consequent association $\{\phi_i\} = \{\psi_i^*\}$ (Winkler, 1977; McCurdy et al., 1980) which leads to the functional of McCurdy et al. (1980). With these assumptions the following relations hold:

$$\rho^{+} = \rho^{*} \qquad \Omega^{+} = \Omega^{*}$$

$$\underline{\Omega}^{+} = \langle \underline{u}|\Omega^{+}|\underline{u}\rangle = \langle \underline{u}^{*}|\Omega^{*}|\underline{u}^{*}\rangle = \underline{\Omega}^{*} \quad \text{(for real } \underline{u}) \qquad (3.28)$$

This leads to $\underline{d}^{\dagger} = \underline{\underline{c}}^{t}$, and the modified bi-orthonormality condition $\underline{\underline{c}}^{t}\underline{\underline{\Delta}}\,\underline{\underline{c}} = \underline{1}$ holds.

We notice that if $\underline{u}$ were complex, then $\underline{\Omega}^{+} \neq \underline{\Omega}^{*}$, $\underline{d}^{\dagger} \neq \underline{c}^{t}$, $\{\phi_i\} = \{\psi_i^{*}\}$ and $\{\psi_i\}$ are not bi-orthogonal any more.

The assumption $\{\phi_i\} = \{\psi_i^{*}\}$ should be considered as a constraint introduced to make the approximate many-electron wavefunction satisfy the same relations as the exact one. This choice permits the construction of a bi-variational SCF program driven by supermatrices (Veillard, 1974) requiring a symmetric density matrix and preserves the associated storage and IO advantages. It just may be that the extraneous enforcement of bi-orthogonality condition is less cumbersome than the coupled iterative solution of Eq. 3.25 and 3.26 in a complex basic set, but it would be interesting to study the proximity of spaces $\{\phi_i\}$ and $\{\psi_i^{*}\}$ where integral driven SCF programs are available. A scheme for such a study is given by Jankowski (1976).

In our numerical investigation we have used a real basic set of symmetry adapted CGTO's and have assumed $\{\phi_i\} = \{\psi_i^{*}\}$. With this assumption $\rho = |\overline{\underline{\Psi}}\rangle_{\text{occ.}}\langle\overline{\underline{\Phi}}|_{\text{occ.}} = |\underline{u}\underline{\underline{c}}\rangle\langle\underline{u}\underline{\underline{c}}^{*}| = |\underline{u}\rangle\underline{\underline{c}}\,\underline{\underline{\tilde{c}}}\langle\underline{u}|$. The convergence criterion $\delta\rho = 0$ demands $\delta(c\tilde{c}) = \underline{0}$. As such, agreement of the real part of the density elements from successive cycles within 1.0×10^{-5} was enforced as a convergence criterion. The stationarity of the total energy was found to be a less sensitive convergence criterion. The generalized eigenvalue Eq. 3.25 was solved using IMSL routine EIGZC (Kaufman, 1975).

Table VIII. Orbital Energies for Beryllium with (4s/2p) Basis Set[†]

	$\alpha = 0.0$	$\alpha = 0.1$	$\alpha = 0.2$
ε_{1s}	- 4.72163	(- 4.7251 -0.0096i)	(- 4.7341 -0.0168i)
ε_{2s}	- 0.30361	(- 0.30517-0.0041i)	(- 0.30973-0.0064i)
ε_{3s}	0.40697	(0.3858 -0.1269i)	(0.3245 -0.2399i)
ε_{4s}	5.48157	(5.191 -1.854i)	(4.333 -3.557i)
ε_{2p}	0.05627	(0.05438-0.0096i)	(0.04879-0.0178i)
ε_{3p}	0.28766	(0.2782 -0.0686i)	(0.2504 -0.1312i)
$E_{Tot.}$	-14.5683	(-14.5743 -0.00457i)	(-14.5865 -0.0227i)

[†] See Table XI for the description of this Basis.

Table VIII - Extended

$\alpha = 0.3$	$\alpha = 0.4$	$\alpha = 0.5$
(- 4.7437 -0.01597i)	(- 4.746 +0.0064i)	(- 2.611 -1.526i)
(- 0.3171 -0.005i)	(- 0.3271 +0.002079i)	(- 1.627 -8.1219i)
(0.2299 -0.3255i)	(0.1130 -0.3725i)	(0.08388-0.7292i)
(2.9461 -4.960i)	(1.0945 -0.0591i)	(0.02867-0.1244i)
(0.03955-0.0228i)	(0.2676 -0.02221i)	(0.05704-0.10087i)
(0.2069 -0.1816i)	(0.15218-0.2126i)	(0.2694 -0.61275i)
(-14.5840 -0.0701i)	(-14.5201 -0.1642i)	(-17.0684 -14.3610i)

Table IX. Orbital Energies for Beryllium with (10s/6p) Basis Set[†]

	α = 0.0	α = 0.1	α = 0.2
1s	- 4.73323	(- 4.7335 +0.000273i)	(- 4.7333 -0.0000597i)
2s	- 0.30912	(- 0.30913+0.000042i)	(- 0.30926 +0.000306i)
3s	0.00195	(0.00190-0.000417i)	(0.001764-0.0008118i)
4s	0.00893	(0.00871-0.00193i)	(0.008066-0.003755i)
9s	0.8525	(0.8242 -0.2125i)	(0.7418 -0.4089i)
10s	6.529	(6.210 -2.119i)	(5.2682 -0.082i)
2p	0.00418	(0.00410-0.0008133i)	(0.00387 -0.0016i)
3p	0.1448	(0.01432-0.002476i)	(0.01386 -0.00496i)
6p	0.30050	(0.2943 -0.06075i)	(0.2759 -0.1190i)
7p	0.7898	(0.7791 -0.1737i)	(0.7207 -0.3374i)
$E_{Tot.}$	-14.57108	(-14.5745 -0.002056i)	(-14.5803 -0.01591i)

[†] Basis Set of Table XI augmented with 6s-type GTO's with exponents given

Table IX - Extended

α = 0.3	α = 0.4	α = 0.5
(- 4.7293 +0.0002217i)	(- 4.717 +0.00629i)	(- 2.5029 -1.5447i)
(- 0.3098 +0.00103i)	(- 0.3117 +0.00245i)	(- 1.0069 -9.4237i)
(0.001544-0.001164i)	(0.001254-0.001455i)	(0.0007396-0.00154i)
(0.007036-0.005376i)	(0.005685-0.006708i)	(0.003423 -0.006876i)
(0.6128 -0.5745i)	(0.4488 -0.6972i)	(0.1724 -0.4221i)
(3.743 -5.732i)	(1.6988 -0.6920i)	(0.2213 -1.1055i)
(0.003493-0.002333i)	(0.002976-0.002986i)	(0.002227 -0.003563i)
(0.01307 -0.007455i)	(0.01179 -0.009963i)	(0.008219 -0.01349i)
(0.2460 -0.1724i)	(0.2058 -0.2187i)	(0.2130 -0.3904i)
(0.62742 -0.4812i)	(0.5049 -0.5952i)	(0.5877 -0.12509i)
(-14.5719 -0.05282i)	(-14.5125 -0.1203i)	(-16.2183 -16.7909i)

by $\left\{\frac{0.52}{n}\right\}_{n=1}^{6}$ and 4p-type GTO's with exponents given by $\{15.56/2.26)^{n}\}_{n=1}^{4}$.

Table X. Orbital Energies for Beryllium with (14s/16p) Basis Set[†]

	$\alpha = 0.0$	$\alpha = 0.1$	$\alpha = 0.2$
ε_{1s}	- 4.73253	(- 4.73257 + 0.0000164i)	(- 4.73269 + 0.000202i)
ε_{2s}	- 0.30926	(- 0.30927 - 0.0000107i)	(- 0.30928 - 0.0000219i)
ε_{3s}	0.00421	(0.00409 - 0.0009281i)	(0.00378 - 0.00180i)
ε_{4s}	0.01957	(0.01904 - 0.004395i)	(0.01749 - 0.00853i)
ε_{13s}	1142.325	(1117.799 - 238.0571i)	(1045.216 - 466.239i)
ε_{14s}	7023.166	(6877.845 -1429.885i)	(6447.731 -2801.663i)
ε_{2p}	0.00007	(0.000066- 0.0000135i)	(0.000062- 0.0000265i)
ε_{3p}	0.00024	(0.000238- 0.0000483i)	(0.000224- 0.0000947i)
ε_{15p}	10.3364	(10.1038 - 2.1787i)	(9.416 - 4.261i)
ε_{16p}	25.4107	(24.836 - 5.405i)	(23.136 - 10.573i)
$E_{Tot.}$	- 14.57261	(- 14.57265 + 0.0000697i)	(- 14.57272 + 0.000235i)

[†] Same as that of McCurdy et al. (1980).

Table X - Extended

α = 0.3	α = 0.4	α = 0.5
(- 4.7329 + 0.000826i)	(- 4.7332 + 0.00279i)	(- 4.7338 + 0.0878i)
(- 0.30931 - 0.0000616i)	(- 0.3094 - 0.000179i)	(- 0.3098 - 0.000531i)
(0.00327 - 0.00257i)	(0.00260 - 0.00320i)	(0.00182 - 0.00365i)
(0.01504 - 0.0121i)	(0.0118 - 0.0151i)	(0.00807 - 0.0171i)
(927.528 - 675.068i)	(769.552 - 855.843i)	(577.62 -1001i)
(5750 -4059i)	(4813.140 -5152.336i)	(3674.476 -6035.401)
(0.000056- 0.000038i)	(0.000047- 0.0000489i)	(0.0000368- 0.0000573i)
(0.000201- 0.000137i)	(0.000169- 0.000174i)	(0.000131- 0.000205i)
(8.302 - 6.154i)	(6.809 - 7.774i)	(4.999 - 9.0439i)
(20.385 - 15.275i)	(16.697 - 19.304i)	(12.2338 - 22.4747i)
(-14.57260 + 0.00064i)	(- 14.5715 + 0.001573i)	(- 14.5672 + 0.003563i)

Table XI. (4s/2p) Contracted Gaussian Basis for Beryllium

s-type

Exponents	Contraction Coefficients
1264.59	0.001945
189.37	0.014835
43.1591	0.072091
12.0987	0.237154
3.80632	0.469199
1.27289	0.35652
3.19646	0.112649
0.747814	0.229506
0.219966	1.0000
0.08231	1.0000

p-type

Exponents	Contraction Coefficients
6.710	0.016378
1.442	0.091553
0.4103	0.341469
0.1397	0.685428
0.0492	1.0000

The beryllium atom was chosen as a first example since the results of these calculations may be used as input for dilated electron propagator study of ^2P shape resonance of Be^- as electron attachment to ^1S Be ground state. Results for basis sets I, II and III (same as that of McCurdy et al., 1980) for various values of α (in radians; $\alpha = \frac{\theta}{1}$) are contained in Tables VIII, IX and X, respectively.

The eigenvalues corresponding to occupied orbitals become essentially real with enlargement of the basis, and the real part of these eigenvalues is always negative, while the eigenvalues corresponding to the unoccupied virtuals are rotated into the fourth quadrant of the complex plane irrespective of the basis set. The ground state total energy, $E_{Tot.} = <\Phi_0|H(\theta)|\Psi_0>$, becomes increasingly real in the same fashion. These features suggest that the Hartree-Fock equations may be analytically continued onto higher Riemann sheets and point to the existence of some self-adjoint operator $\Omega'(0)$ $(=\Omega(0)?)$ whose transformation $\Omega(\theta)$ may be considered (Weiner, 1981). We note that for smaller basis sets I and II there is a complete breakdown of the dilatation analytic picture of $\Omega(\theta)$ for $\alpha = 0.5$ radians.

Surprisingly, the distinction between the occupied and unoccupied orbitals is maintained even with the smallest basis set since the spectrum remains strongly reminiscent of the spectrum of rotated self-adjoint operators. Perfect bi-orthonormality was obtained in each case. The use of real basis sets makes possible the use of existing integral packages without any modifications, and the flow of logic for two-electron integral transformation is kept intact. The use of bi-variational SCF in a reasonably good basis set capped by the construction of a dilated electron propagator in the bi-orthonormal orbital basis set so generated for the calculation of shape and Feshbach resonances thus becomes a powerful and tempting alternative to other schemes (McCurdy et al., 1980; Donnelly and Simons, 1980). The construction of the dilated electron propagator is described in the next section.

3.3 The Dilated Electron Propagator

The bi-variational SCF furnishes the bi-orthonormal sets $\{\phi_i\}$ and $\{\psi_i\}$, and N occupied orbitals determine Φ_0 and Ψ_0. For the ideal case of complete spin-orbital bases $\{\phi_i\}$ and $\{\psi_i\}$ the closure relation becomes

$$\delta(x-x') = \sum_k \phi_k^*(x')\psi_k(x) \tag{3.29}$$

x being a compound space spin coordinate.

We can write the appropriate zeroth order density operator as

$$\rho_0 = |\Psi_0\rangle\langle\Phi_0| \tag{3.30}$$

with

$$\mathrm{Tr}\rho_0 = 1 \tag{3.31}$$

and

$$E = \langle H\rangle = \mathrm{Tr}\{H\rho_0\} \tag{3.32}$$

being stationary. The exact ground state solution can be represented by the density operator $\rho = \rho_0 + (\rho - \rho_0)$ (Nehrkorn et al., 1976). The space of all antisymmetric tensors of different ranks corresponding to state-vectors representing different numbers of particles generated by the set $\{\psi_i\}$, under natural linear operations and exterior multiplications $\wedge$ which increase the rank of the tensors, constitutes a Grassmann Algebra G. We also introduce the adjoint algebra G*, and in terms of the duality <,> between G and G*, the interior multiplication of the left $\lrcorner$, and of the right L, are defined as follows:

$$<x,a_i\wedge\eta> \; = \; <x(a_i\wedge)^+,\eta> \; = \; <x\lrcorner a_i,\eta> \qquad (3.33)$$

with x, $x\lrcorner a_i$ ε G* and η, $a_i\wedge\eta$ ε G. Similarly we have

$$<x\wedge a^i,\eta> \; = \; <x,(\wedge a^i)^+\eta> \; = \; <x,a^i L\eta> \qquad (3.34)$$

x, $x\wedge a^i$ ε G* and η, $a^i L\eta$ ε G.

The interior multiplications $a^i L$ and $\lrcorner a_i$ decrease the rank of tensors in G and G*, respectively. It is obvious that the exterior multiplications $a_i\wedge$ and $\wedge a^i$ and the interior multiplications $a^i L$ and $\lrcorner a_i$ may be formalized as the familiar creation and annihilation operators on the direct $\{\psi_i\}$ and adjoint $\{\phi_i\}$ spaces, respectively, except that now the operators and their adjoints do not have to have the same domain. Specifically $(a_i\wedge)^+ = \lrcorner a_i$. These concepts are part of the general theory of Dual Grassmann Algebras (Froelich, 1980b). We cite some other relevant results:

$$(a_i\wedge)^+ \; = \; \lrcorner a_i \qquad\qquad (a^i L)^+ \; = \; \wedge a^i \qquad (3.35)$$

$$[a^i L,a^j L]_+ \quad 0 \; = \; [a_i\wedge,a_j\wedge]_+ \qquad [a_i\wedge,a^j L]_+ \; = \; \delta_{ij} \qquad (3.36)$$

We define the electron field operators $\hat{\psi}(x)$ for the direct space

$$\hat{\psi}(x) \; = \; \sum_i \psi_i(x)\; a^i L \qquad (3.37)$$

$$= \; \sum_i \psi_i\,(x)\;(\wedge a^i)^\dagger \qquad (3.38)$$

and $\underset{\sim}{\hat{\psi}}^{\dagger}(x)$ for the adjoint space

$$\underset{\sim}{\hat{\psi}}^{\dagger}(x) = \sum_{i} \phi_i^{*}(x)\ (\lrcorner a_i)^{\dagger} \tag{3.39}$$

$$= \sum_{i} \phi_i^{*}(x) a_i \wedge \tag{3.40}$$

and in terms of the duality between G and G*, generalize the regular second-quantized representation of the physical operators, e.g., for the dilated Hamiltonian from Eq. 3.12, written as

$$H(\theta) = \sum_{i=1}^{N} h_i(\theta) + \tfrac{1}{2} \sum_{i} \sum_{j \neq i} g_{ij}(\theta) \tag{3.41}$$

$$H(\theta) = \int \underset{\sim}{\hat{\psi}}^{\dagger}(x_1) h_1(\theta) \hat{\psi}(x_1) dx_1 + \tfrac{1}{2} \int \underset{\sim}{\hat{\psi}}^{\dagger}(x_1) \underset{\sim}{\hat{\psi}}^{\dagger}(x_2)$$

$$\times\ g_{12}(\theta) \hat{\psi}(x_2) \hat{\psi}(x_1) dx_1 dx_2 \tag{3.42}$$

$$= \sum_{r} \sum_{s} \langle \phi_r | h(\theta) | \psi_s \rangle\ a_r \wedge a^{s} L + \tfrac{1}{2} \sum_{r} \sum_{r'} \sum_{s} \sum_{s'}$$

$$\times \langle \phi_r \phi_{r'} | g(\theta) | \psi_s \psi_{s'} \rangle\ a_r \wedge a_{r'} \wedge a^{s'} L a^{s} L \tag{3.43}$$

We note that the number operator for electrons will be

$$N_{op} = \sum_{r} a_r \wedge a^{r} L = \sum_{r} n_r \tag{3.43}$$

and the occupation numbers are

$$\mathrm{Tr}\{\rho_0 a_r \wedge a^{r} L\} \equiv \langle n_r \rangle = \begin{cases} 1 \text{ if } \psi_r \text{ occupied in } \Psi_0 \\ 0 \text{ otherwise} \end{cases} \tag{3.44}$$

We partition the Hamiltonian in Eq. 3.43 as

$$H(\theta) = H_0(\theta) + V(\theta) \tag{3.46}$$

where

$$H_0(\theta) \;=\; \sum_k \varepsilon_k a_k \wedge a^k L \qquad (3.47)$$

and

$$V(\theta) \;=\; \sum_i \sum_j \sum_k \sum_\ell <\phi_i\phi_j||\psi_k\psi_\ell>[\tfrac{1}{4}a_i \wedge a_j \wedge a^\ell L a^k L \;-\; \delta_{j\ell}<n_\ell>a_i \wedge a^k L] \qquad (3.48)$$

with

$$<\phi_i\phi_j||\psi_k\psi_\ell> \;\equiv\; <\phi_i\phi_j|g(\theta)|\psi_k\psi_\ell> - <\phi_i\phi_j|g(\theta)|\psi_\ell\psi_k> \qquad (3.49)$$

The linear space of fermionlike creation and annihilation operators introduced in the super-operator formulation of the propagator equations (Goscinski and Lukman, 1970) is now to be replaced by bi-orthonormal operator spaces

$$\underline{h} \;=\; \{a^i L, a_i \wedge a^j L a^k L, \ldots\} \qquad j<k \qquad (3.50)$$

$$\underline{\tilde{h}} \;=\; \{\lrcorner a_i, \lrcorner a_k \lrcorner a_j \wedge a^i, \ldots\} \qquad j>k \qquad (3.51)$$

with scalar product

$$(\tilde{h}_i|h_j) \;\equiv\; \mathrm{Tr}\{[h_j,\tilde{h}_i^\dagger]_+\rho\} \qquad (3.52)$$

We define super-operator Hamiltonian

$$\hat{H}(\theta) \;=\; \hat{H}_0(\theta) + \hat{V}(\theta) \qquad (3.53)$$

and the super-operator identity $\hat{I}$ satisfying the relations (Goscinski and Lukman, 1970; Pickup and Goscinski, 1973)

$$\hat{H}_0 X = [X, H_0(\theta)]_- \qquad \hat{V}X = [X, V(\theta)]_- \tag{3.54}$$

$$\hat{I}X = X \qquad \forall\, X \in \underline{h} \tag{3.55}$$

Analogous to the previous treatments (Pickup and Goscinski, 1973), the Fourier transformed equation of motion of the dilated electron propagator (Eq. 3.10) may now be written as

$$\underline{G}(\theta) = (\underline{\tilde{a}}|(E\hat{I} - \hat{H}(\theta))^{-1}\underline{a}) \tag{3.56}$$

for the electron propagator, i.e., a matrix with elements

$$G_{ij}(\theta) = (\tilde{a}_i|(E\hat{I} - \hat{H}(\theta))^{-1}|a^j) \tag{3.57}$$

where $\tilde{a}_i = Ja_i$, and $a^j = a^jL$.

Approximation schemes can now be developed exactly as in earlier work (Öhrn, 1976, 1978), and instead of expression Eq. 3.46, we study

$$\underline{G}(\theta) = (\underline{\tilde{a}}|\underline{h})(\underline{\tilde{h}}|(E\hat{I} - \hat{H}(\theta))h)^{-1}(\underline{\tilde{h}}|\underline{a}) \tag{3.58}$$

obtained by inner projection (Pickup and Goscinski, 1973).

The zeroth order expression for the electron propagator is obtained by using ρ_0 from Eq. 3.30 as the density operator,

$$\underline{h} = \underline{h}^1 = \{a^iL\} \qquad \text{and} \qquad \underline{\tilde{h}} = \underline{\tilde{h}}^1 \equiv \{Ja_i\} \tag{3.59}$$

in

$$\underline{G}^0(\theta) = (\underline{\tilde{a}}|(E\hat{I} - \hat{H}(\theta))\underline{a})^{-1} \tag{3.60}$$

i.e.,

$$G^0_{ij}(\theta) = \delta_{ij}/(E - \varepsilon_i) \tag{3.61}$$

This demonstrates the equivalence of this development to that of the unrotated propagator. The structural equivalence at any order of perturbation theory between the dilated propagator $\underline{G}(\theta)$ and the unrotated case, demonstrated by the corresponding choice of projection manifolds and density operators, guarantees the ease with which the dilated propagator coalesces into the undilated one for $\theta = 0$ at any level of approximation. For example, choosing $\rho = \rho_0$, $\underline{h} = \underline{h}^1 \oplus \underline{h}^3$, and $\underline{\tilde{h}} = \underline{\tilde{h}}^1 \oplus \underline{\tilde{h}}^3$, with

$$\underline{h}^3 = \{a_\alpha \wedge a^p L a^q L, a_p \wedge a^\alpha L a^\beta L\} \tag{3.62}$$

($\alpha<\beta$ labeling occupied, $p<q$ labeling unoccupied orbitals, and i,j labeling unspecified orbitals) and

$$\underline{\tilde{h}}^3 = \{\lrcorner a_q \lrcorner a_p \wedge a^\alpha, \lrcorner a_\beta \lrcorner a_\alpha \wedge a^p\} \tag{3.63}$$

we can write (Pickup and Goscinski, 1973)

$$\underline{G}^{-1}(\theta) = E\underline{I} - \underline{\varepsilon} - \underline{\Sigma}(\theta) \tag{3.64}$$

where the self-energy matrix is

$$\underline{\Sigma}(\theta) = (\underline{\tilde{a}}|\hat{H}(\theta)h^3)(\underline{\tilde{h}}^3|(E\hat{I} - \hat{H}(\theta))h^3)^{-1}(\underline{\tilde{h}}^3|\hat{H}(\theta)\underline{a}) \tag{3.65}$$

Through second order in electron interaction we obtain

$$\Sigma^2_{ij}(\theta) = \tfrac{1}{2}\sum_\alpha \sum_p \sum_q \frac{<\phi_p\phi_q||\psi_i\psi_\alpha><\phi_j\phi_\alpha||\psi_p\psi_q>}{E+\varepsilon_\alpha-\varepsilon_p-\varepsilon_q} + \tfrac{1}{2}\sum_\alpha \sum_\beta \sum_p \frac{<\phi_\alpha\phi_\beta||\psi_i\psi_p><\phi_j\phi_p||\psi_\alpha\psi_\beta>}{E+\varepsilon_p-\varepsilon_\alpha-\varepsilon_\beta} \tag{3.66}$$

This expression for the second order self-energy differs from that of

Donnelly and Simons (1980) because of a different partitioning of the Hamiltonian. The expression of Winkler (1977) was derived with the assumption that $\{\phi_i\} = \{\psi_i^*\}$, and the so-called c-symmetry (Moiseyev et al., 1978) was employed. Yet, the self-energy expression of Winkler does not revert to the unrotated Σ_{ij}^2 for $\theta = 0$, and could be in error.

We note that except for the bi-orthogonality, the expression in Eq. 3.66 is remarkably similar to the unrotated Σ_{ij}^2 expression, and since for $\theta = 0$, $\{\phi_i\} = \{\psi_i\}$, it will be identical to the standard expression (Pickup and Goscinski, 1973). It is obvious that retention of $\hat{H}$ instead of its approximation by $\hat{H}_0$ in the inverse matrix in Eq. 3.65 will result in the equivalent of the full 2p-h TDA approximation (Schirmer and Cederbaum, 1978a; Born and Öhrn, 1979; Mishra and Öhrn, 1980a) for the dilated propagator. The ease of extensions to mimic the higher order decouplings of Redmon et al. (1975) or the advantages that accrue from the approximation of Kurtz and Öhrn (1978) need hardly be stressed.

The approach outlined provides a general theoretical format for the construction of the infinite order or the renormalized dilated electron propagator and allows for simple, systematic and easily cognizable approximation schemes. No assumption about the sufficiency of first order correction to the variational ground state, as a means of accommodating rotation effects or the applicability of the perturbation theory to the perturbation Hamiltonian $V(\theta) = H(\theta) - F(\theta=0)$, where F is the Fock operator (Donnelly and Simons, 1980) need be made. The second order approximation of Winkler (1977) is recovered easily and without invoking other supplementary concepts like the c-product. The scheme is comprehensive and permits the treatment of cases where $\{\phi_i\} = \{\psi_i^*\}$ is not a good approximation (Froelich, 1980a). All the standard decoupling procedures for the unrotated propagator may be easily incorporated.

We notice that Eq. 3.64 may be rewritten as

$$\underline{G}^{-1}(\theta,E) = E\underline{I} - \underline{L}(\theta,E) \qquad \underline{L} = \underline{\varepsilon} + \underline{\Sigma} \tag{3.67}$$

and following Layzer (1963) the poles of the dilated electron propagator are the energy dependent eigenvalues of the equation

$$\underline{L}(\theta,E)X_n(\theta,E) = E_n(\theta,E)X_n(\theta,E) \tag{3.68}$$

The pole search scheme of Donnelly and Simons (1980) which involves an iterative solution of Eq. 3.68 is quite satisfactory and may be incorporated in toto. The difference between their scheme and the one presented here can now be easily identified as the difference in the choice of the unperturbed Hamiltonian and the attendant orbital manifold employed for the construction of $\underline{L}$.

The recent results of McCurdy et al. (1980) indicate that the shape resonances can be treated at the bi-variational SCF level. Feshbach resonances which involve more intricate correlation and relaxation effects are, however, poorly described, and the bi-variational ΔSCF does not furnish their lifetime.

This success of the bi-variational SCF scheme to predict resonances points to the optimal nature of the bi-variationally obtained bi-orthonormal orbital manifold for the construction of the dilated electron propagator. The ease of incorporating correlation effects to desired levels would make possible a unified treatment of shape and Feshbach resonances.

Our numerical investigation of the bi-variational SCF procedure shows that the CPU and storage requirements are comparable to those for the ordinary SCF schemes and are entirely manageable. Since the four index transformation packages (Roos, 1974) always utilize separate partial transformation of the two indices on the right followed by those on the left, the transformation of two-electron integrals $<\kappa\lambda|\mu\nu>$ over the primitive computational basis set into $<\phi_k\phi_\ell|\psi_m\psi_n>$ would involve minimal changes in the logic of transformations, and the modifications to handle the complex arithmetic should not be overly formidable. Once the transformed two-electron integrals are available, due to the ease of the attendant order analysis, the construction of $\underline{\Sigma}$, and consequently $\underline{L}$, would be much simpler. It may so happen that with increased computational experience in the implementation of this scheme, one would discover a few energy dependent eigenvalues of $\underline{L}$ to be entirely stable with respect to changes in $\theta>\theta_{res}$, and the need for extensive θ-trajectory calculations could be supplanted by the ease of iterative solution of Eq. 3.68 for the appropriate symmetry block of $\underline{L}$ for a few $\theta>\theta_{res}$ and identification of these stable eigenvalues with shape and Feshbach resonances. The speed with which iterative solution of Eq. 3.68 was found to converge (Donnelly and Simons, 1980) is most encouraging.

Summing up, notwithstanding the slowness of the complex arithmetic involved, this procedure should certainly be manageable for the kind of systems to which this methodology is being employed and is warranted by the fundamental role of bi-orthogonality in non-hermitean problems. Innate rigour and wider applicability should further compensate the loss of speed.

EPILOGUE

The principal objective of this dissertation has been the formulation of theoretical schemes for a correlated treatment of bound-continuum transitions. The schemes fabricated obviate many limitations of earlier attempts and could serve as tools for an improved understanding of various aspects of the bound-continuum transitions within a general and rigorous theoretical framework. While the full 2p-h TDA has been studied in some detail and criteria for its efficacy and dependability have been established, the OPW and the dilated electron propagator formulations have not been investigated numerically. The numerical groundwork for these two schemes has, however, produced encouraging results. A detailed computational investigation of these schemes is an obvious extension of this work.

Throughout, the formalism assumes closed shell reference states. The open shell reference states may be described within the framework established here, if a spin unrestricted Hartree Fock description for the reference state is deemed adequate. This less satisfactory feature may be mitigated by the use of a unitary group approach to the open shell electron propagator proposed recently (Born and Shavitt, 1980). Due to the non-dilatation analyticity of the Born-Oppenheimer Hamiltonian, no attempt at the description of molecular resonances has been made. Some recent schemes (McCurdy and Rescigno, 1978; Simon, 1979) seem promising in this connection, and results obtained (Rescigno et al., 1980) are very encouraging.

APPENDIX

We have used the following identities (Harris, 1973)

$$\exp(\pm i\vec{k}\cdot\vec{R}_{pq}) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (\pm i)^{\ell} j_{\ell}(kR_{pq}) \mathcal{Y}_{\ell m}(\theta_k,\phi_k) \mathcal{Y}_{\ell m}(\theta',\phi') \qquad (A.1)$$

$$= 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (\pm i)^{\ell} j_{\ell}(kR_{pq}) Y^{*}_{\ell m}(\theta_k,\phi_k) Y_{\ell m}(\theta',\phi') \qquad (A.2)$$

where $\mathcal{Y}_{\ell m}$ and $Y_{\ell m}$ denote real and complex spherical harmonics (Edmonds, 1974), respectively; (θ_k,ϕ_k) and (θ',ϕ') describe the directions of $\vec{k}$ and $\vec{R}_{pq}$, respectively. When $\vec{R}_{pq}$ coincides with the molecular z-axis (A.1) reduces to

$$\exp(\pm i\vec{k}\cdot\vec{R}_{pq}) = (4\pi)^{\frac{1}{2}} \sum_{\ell} (\pm i)^{\ell} j_{\ell}(kR_{pq})(2\ell+1)^{\frac{1}{2}} \mathcal{Y}_{\ell 0}(\theta_k,\phi_k)$$

$$\mathcal{Y}_{\ell 0} = Y_{\ell 0} \qquad (A.3)$$

Implicit in this reduction is the addition theorem

$$P_{\ell}(\cos\theta) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} \mathcal{Y}_{\ell m}(\theta',\phi') \mathcal{Y}_{\ell m}(\theta'',\phi'') \qquad (A.4)$$

$$= \frac{4\pi}{2\ell+1} \sum_{m} Y^{*}_{\ell m}(\theta',\phi') Y_{\ell m}(\theta'',\phi'') \qquad (A.5)$$

where θ is the angle between directions represented by (θ',ϕ') and (θ'',ϕ''). It follows that

$$\cos\theta = P_1(\cos\theta) = \frac{4\pi}{3}\sum_{m=-1}^{1} \mathcal{Y}_{1m}(\theta',\phi')\mathcal{Y}_{1m}(\theta'',\phi'') \qquad (A.6)$$

$$= \frac{4\pi}{3}\sum_{m=-1}^{1} Y^*_{1m}(\theta',\phi')Y_{1m}(\theta'',\phi'') \qquad (A.7)$$

The Clebsch-Gordan coefficients are defined by (Harris, 1973)

$$C^{m_1m_2m}_{\ell_1\ell_2\ell} = \int \mathcal{Y}_{\ell_1m_1}(\Omega)\mathcal{Y}_{\ell_2m_2}(\Omega)\mathcal{Y}_{\ell m}(\Omega)d \qquad (A.8)$$

$$C^{mm_1m_2}_{\ell\ell_1\ell_2} = \int Y^*_{\ell m}(\Omega)Y_{\ell_1m_1}(\Omega)Y_{\ell_2m_2}(\Omega)d \qquad (A.9)$$

and the orthogonality relation for the spherical harmonics is given by

$$\int \mathcal{Y}_{\ell_1m_1}(\Omega)\mathcal{Y}_{\ell_2m_2}(\Omega)d\Omega = \delta_{\ell_1\ell_2}\delta_{m_1m_2} \qquad (A.10)$$

$$\int Y^*_{\ell_1m_1}(\Omega)Y_{\ell_2m_2}(\Omega)d\Omega = \delta_{\ell_1\ell_2}\delta_{m_1m_2} \qquad (A.11)$$

$$Y^*_{\ell m}(\Omega) = (-)^m\, Y_{\ell,-m} \qquad (A.12)$$

The coupling rule for the rotation matrices is

$$D^{\ell_1}_{m_1,m_1'}\,D^{\ell_2}_{m_2,m_2'} = \sum_j C^{m_1m_2m_1+m_2'}_{\ell_1\ell_2j}\,C^{m_1'm_2'm_1'+m_2'}_{\ell_1\ell_2j}\,D^j_{m_1+m_2,m_1'+m_2'} \qquad (A.13)$$

and the complex conjugate of a matrix element is given by

$$D^{*\ell}_{m',m} = (-)^{m'-m}\,D^{\ell}_{-m',-m} \qquad D^{0*}_{00} = 1 \qquad (A.14)$$

The following integrals are useful:

$$\int\int\int \sin\beta d\beta d\alpha d\gamma \; D^{\lambda *}_{\mu,\nu}(\underline{B}) D^{\ell}_{m,n}(\underline{B}) \;=\; 8\pi^2 (2\ell+1)^{-1} \delta_{\ell,\lambda}\delta_{\mu,m}\delta_{\nu,n} \qquad (A.15)$$

$$\int\int\int \sin\beta d\beta d\alpha d\gamma \;=\; 8\pi^2 \qquad (A.16)$$

The Fourier transforms (Kaijser and Smith, 1977) $\xi_\ell(\vec{k})$ may be written as

$$\xi_\ell(\vec{k}) \;=\; F_\ell(k) \sum_i c_i^\ell \mathcal{Y}_{\ell_i m_i}(\theta_k,\phi_k) \qquad (A.17)$$

$$\;=\; F_\ell(k) \sum_i c_i^\ell Y_{\ell_i m_i}(\theta_k,\phi_k) \qquad (A.18)$$

whereby

$$\xi_\ell(\vec{k})\xi_m^*(\vec{k}) \;=\; F_\ell(k)F_m^*(k) \sum_i \sum_j c_i^\ell c_j^m \mathcal{Y}_{\ell_i m_i}(\theta_k,\phi_k)\mathcal{Y}_{\ell_j m_j}(\theta_k,\phi_k)$$

$$\;=\; F_\ell(k) \sum_i \sum_j c_i^\ell c_j^m \sum_{L=|\ell_i-\ell_j|}^{\ell_i+\ell_j} C_{L\ell_i\ell_j}^{Mm_im_j} \mathcal{Y}_{LM}(\theta_k,\phi_k) \qquad (A.19)$$

$$\;=\; F_\ell(k)F_m^*(k) \sum_i \sum_j c_i c_j^{m*} Y_{\ell_i m_i}(\theta_k,\phi_k)Y_{\ell_j m_j}(\theta_k,\phi_k)$$

$$\;=\; F_\ell(k)F_m^*(k) \sum_i \sum_j \sum_{L=|\ell_i-\ell_j|}^{\ell_i+\ell_j} c_i^\ell c_j^{m*} C_{L\ell_i\ell_j}^{Mm_im_j} Y_{LM}(\theta_k,\phi_k) \qquad (A.20)$$

We evaluate the integral $\int \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(k)\xi_q^*(k)d\Omega$ for a linear molecule with $\vec{R}_{pq}$ along the z-axis. For non-linear molecules, similar expressions apply employing appropriate rotation matrices (Schweig and Thiel, 1974). The integral is easily evaluated when $\vec{R}_{pq} = \vec{0}$, so we treat the case $\vec{R}_{pq} \neq \vec{0}$ using (A.3), (A.8), (A.17) and (A.19) :

$$\int \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q(\vec{k})d\Omega \;=\; (4\pi)^{\frac{1}{2}}\, F_p(k)F_q^{*}(k) \sum_i \sum_j \sum_{\ell=|\ell_i-\ell_j|}^{\ell_i+\ell_j}$$

$$\times\; c_i^p c_j^q(-i)^{\ell}\, j_{\ell}(kR_{pq})(2\ell+1)^{\frac{1}{2}}\, C_{\ell\ell_i\ell_j}^{0m_im_j} \qquad (A.21)$$

We evaluate the integral $\int \cos\theta_{\vec{m}_p,\vec{k}}\, \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(\vec{k})\xi_q^{*}(\vec{k})d\Omega$ using (A.3), (A.6), A.8), (A.17) and (A.19):

$$\int \cos\theta_{\vec{m}_p,\vec{k}}\, \exp(-i\vec{k}\cdot\vec{R}_{pq})\xi_p(k)\xi_q^{*}(k)d\Omega \;=\; \frac{(4\pi)^{3/2}}{3}\, F_p(k) \sum_i \sum_j \sum_{L=|\ell_i-\ell_j|}^{\ell_i+\ell_j}$$

$$\times \sum_{\ell=|L-1|}^{L+1} (-i)^{\ell}\, j_{\ell}(kR_{pq})(2\ell+1)^{\frac{1}{2}}$$

$$\times\; c_i^p c_j^q$$

$$\times \sum_{n=-1}^{1} Y_{1n}(\theta_{\vec{m}_p}, \phi_{\vec{m}_p})\, C_{L1\ell}^{nn0}\, C_{L\ell_i\ell_j}^{nm_im_j}$$

$$(A.22)$$

where

$$\theta_{\vec{m}_p} = \cos^{-1}\left(\frac{\vec{m}_p^{\,z}}{|\vec{m}_p^{\,x}|}\right) \qquad (A.23)$$

$$\phi_{\vec{m}_p} = \tan^{-1}\left(\frac{\vec{m}_p^{\,y}}{\vec{m}_p^{\,x}}\right) \qquad (A.24)$$

The superscripts x,y,z denote the various components of the vector $\vec{m}_p$.

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BIOGRAPHICAL SKETCH

Manoj Kumar Mishra was born on October 15, 1952, in Begusarai, Bihar, India. He graduated from Modern High School, New Delhi, in 1968, where he was an All India Merit Scholar from 1964 to 1968. He received his B.Sc. (honors) degree in 1972 from St. Xavier's College, Ranchi University. He was a National Merit Scholar at the Indian Institute of Technology, Delhi, from 1972 to 1974 and was awarded the Certificate of Merit (1973) and the M.Sc. degree (1974) by this institution. During the year of 1974-1975 he was an UGC Junior Research Fellow at the School of Life Sciences, Jawaharlal Nehru University, New Delhi. He has been a graduate student with the Chemistry Department of the University of Florida since Fall 1975 and was awarded an additional fellowship by the Graduate School for the academic year 1979-80. Since Spring 1978 he has been a research assistant to Professor N. Y. Öhrn and has co-authored four research papers under his guidance.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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Professor of Chemistry and Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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